

Original Research Article

Synthesis of New Polyurethanes Based on 2,3-Dihydro-1,4-Phthalazinedione

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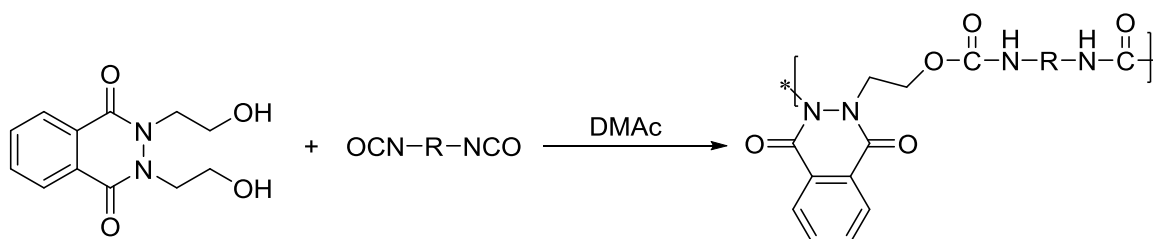
Thermal analysis

Differential thermal gravimetric analysis

ABSTRACT

In this work, to synthesis the 2-(2-hydroxy ethyle)-2,3-dihydro-1,4-phthalazinedione and 2,3-bis(2-hydroxyethyle)-2,3-dihydro-1,4-phthalazinedione, 2-boromoethanol was reacted with phthalhydrazide in DMAc at presence of triethylamine in mole ratio of 1.5:1 and 3:1 respectively. The structure of the monomers was evaluated using the IR and ¹H-NMR spectra. New polyurethanes were synthesized by reaction of the monomers with various diisocyanates including, tolylene diisocyanate, isophorane diisocyanate and hexamethylene diisocyanate. The measured viscosity for these polymers was found to be at the range of 0.45-0.6 dl^g⁻¹. The structure of the polymers was proved by IR, ¹HNMR spectra and CHN analysis. The TGA and DTG results confirmed high thermal stability for the synthesized polymers.

GRAPHICAL ABSTRACT



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Introduction

Phthalate hydrazide (2,3,3-dihydro-1,4-phthalazine diavone) is a two-functional, heterocyclic, nucleophilic compound. This compound contains two relatively acidic protons which are useful for reacting with two-functional compounds [1]. Phthalazine rings are widely used in organic synthesis and pharmaceutical compounds [2] and their pharmacological properties have been particularly proven in cardiovascular diseases [3]. Phthalazine has been known to be the central nucleus of many drug compounds with anti-cancer [4], anti-hypertensive [5], anti-clotting [6], anti-inflammatory [7], and diabetes treatment activities [8]. The compound bis (phthalazin-1-1-hydrazone) -2,6-diacetylpyridine was synthesized by researchers in 2014 and used as a ligand in copper, cobalt and nickel complexes. These complexes have high antimicrobial properties.

This reaction is carried out in three steps. In the first step, arine was prepared from ortho-(trimethylsilyl) aryl triflate at the presence of the cesium fluoride. Then the direct acetylalkylation of arine by β -ketoester was performed in acetonitrile solvent and the compound was synthesized. This compound was converted to the corresponding diazo by *para*-acetamido salt of benzene sulfonyl azide (*p*-ABSA) in acetonitrile at room temperature. At final step, the Wittig reaction and ring closure were carried out using the di-isopropyltriobutyl phosphine and finally phthalazine was synthesized [9].

Besides, the analysis suggests that not only the synthesized polymers have favorable polymer properties such as acceptable viscosity range and high thermal resistance, but also these polymers, due to the presence of phthalazine nucleus in their structure, may have medical applications as well [10].

Polyurethanes are a group of elastomeric polymers formed by the increasing reaction

between the isocyanate functional group [11]. Polyurethane chains are usually composed of two flexible segments (soft segments) and elastic and relatively rigid segments whose ratios determine the mechanical properties of the polymer including tensile properties, crystallization temperature and melting point [12]. Diol chain length, diisocyanate space chemistry and catalyst are effective in determining the ratio of hard and soft segments [13]. Usually, soft, amorphous, and glass transition temperatures are lower than room temperature, resulting in polymer molding. The hard, crystalline and hydrogen bonded portions are glass transition temperatures between 50 °C and 100 °C, which give the polymers strength and resistance to the design [14]. In the reaction of isocyanates with alcohols, the concentration of the reactants alone does not determine the rate. Studies on the role of the solvent have shown that three solvent properties including polarity, ability to form hydrogen bonds and dielectric constant at effective reaction speed [11].

Polyurethane and its derivatives are the most widely used polymers in various industries around the world. The formulation of this polymer is such that it encompasses a wide range of hard, dry and compact materials [16]. Hard polyurethane foams have low density, high strength, high adhesion strength and wear resistance which are used in various industrial fields such as pipelines, automotive and aircraft industries [17,18]. The viscoelastic foams of these polymers are used in building panels as thermal insulation, sound and vibration [19-21]. Biodegradable polyurethanes are strategic compounds that, due to their versatility and wide range of mechanical and physical properties, have enabled the production of biological materials such as implants, vascular prostheses, artificial skin and tissue scaffolds [22-25]. For example, in recent years, a number of smart polyurethanes (low-density memory polymers) have been used to treat the embolism [26]. The

optics, paint and resin and textile industries are also industries where polyurethane applications can be mentioned [27]. Some disadvantages of the polyurethanes, such as biodegradation and flammability and the production of toxic gases in the event of a fire, have led researchers to always look for ways to improve the properties of these polymers.

In this study, the synthesis of phthalazine-1,4-dions was performed by reaction of 3-chloro phthalic anhydride with methylhydrazide in the presence of montmorillonite. Phthalazine-1,4-Dions desired with 1,3-dibromo-propane reacted with potassium carbonate in DMF solvent for two hours at room temperature, and *N, N*-dialkyl-5-chloro-2,3-dihydehyde 1,4-D-DNAs and were synthesized. Finally, the reaction of these compounds with NaN_3 and NaI in DMSO solvent was obtained [15].

Experimental

All material were purchased from Fluka and Merck used without purification. ^1H NMR spectra were recorded on a 500 MHz Bruker Advance XRD instrument using DMSO-d_6 as solvent and tetramethylsilane as an internal standard. FTIR spectra were recorded using a Bruker Vector 22

spectrometer on KBr pellets. The CHN-600 Lecoanalyzer was used for elemental analysis. Thermal gravimetric analysis (TGA) of the polyurethanes were done. Inherent viscosity ($\eta_{\text{inh}} = L \eta_{\text{rel}} / C$) of the polymers were determined for solution of 0.5 g/dl in NMP at 25 °C using an Ostwald viscometer.

Preparation of Monomers

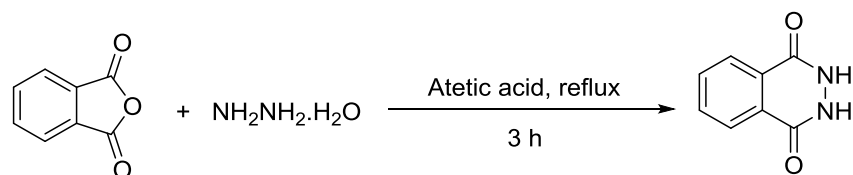
Synthesis of 2,3-dihydro-1,4-phthalazinedione

This compound was synthesized from the reaction of phthalic anhydride with hydrazine hydrate in acetic acid solvent (Scheme 1).

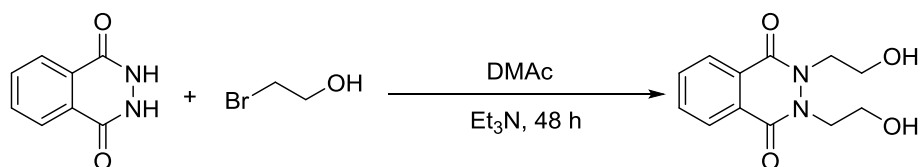
2,3-dihydro-1,4-phthalazinedione: IR(KBr, cm^{-1}): ν 3200(NH), 1660(C=O), 790(C=C Aro.)

Synthesis of 2,3-bis(2-hydroxy ethyl)-2,3-dihydro-1,4-phthalazinedione

This compound was synthesized from the reaction of phthal hydrazide with 2-equivalant-bromoethanol in *N, N*-dimethylacetamide solvent for 48 h (Reflux) (Scheme 2).



Scheme 1. Synthesis reactions for preparation of 2, 3- dihydro- 1, 4-phthalazinedione

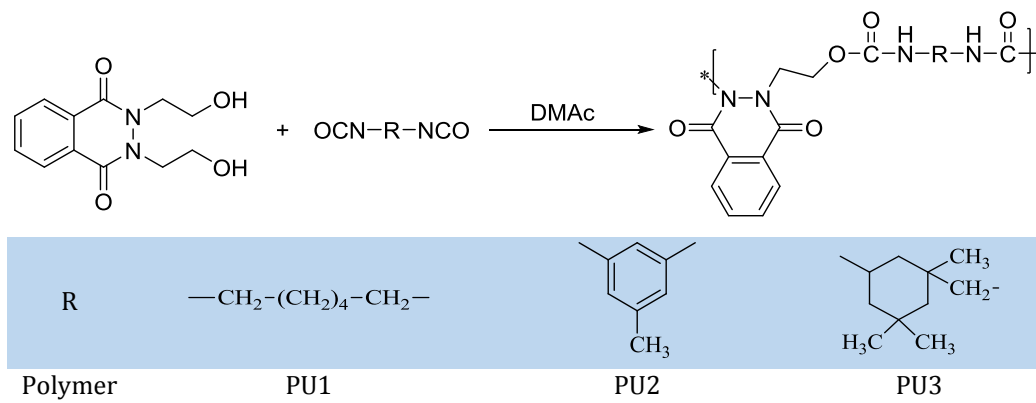


Scheme 2. Synthesis reactions for preparation of 2,3-bis(2-hydroxy ethyl)-2,3-dihydro-1,4-phthalazinedione

Preparation of Polyurethanes

These polymers were synthesized from the reaction of synthesis of 5,6,7,8-tetrabromo-2,3-bis(2-hydroxyethyl)-2,3-dihydro-1,4-phthalazine-dione with different diisocyanate such as

Hexamethylenediisocyanate, Toloylenediisocyanate, Isofurenediisocyanate, Methylenediphenyldiisocyanate and 1,4-phenylenediisocyanate with a Equal to the molar amount in dimethyl acetamide solvent (Scheme 3).



Scheme 3. Synthesis reactions for preparation of polymers

Figure 1. TGA spectra of PU1

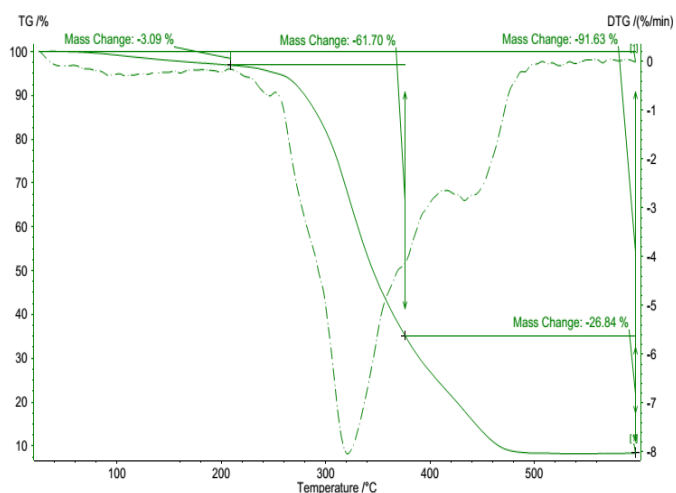


Figure 2. TGA spectra of PU2

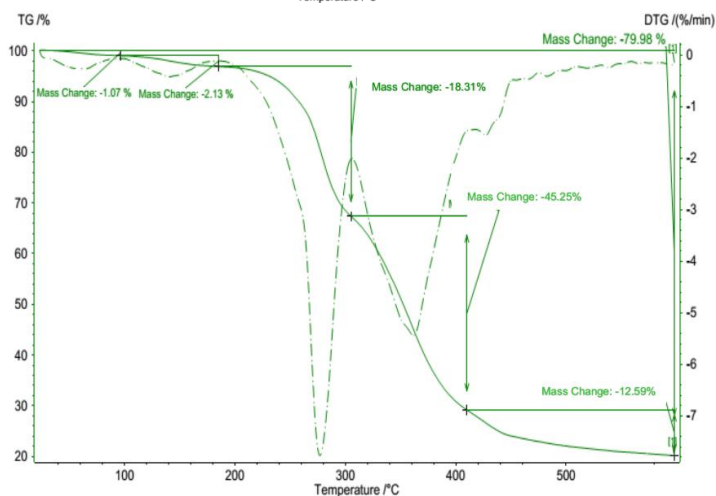
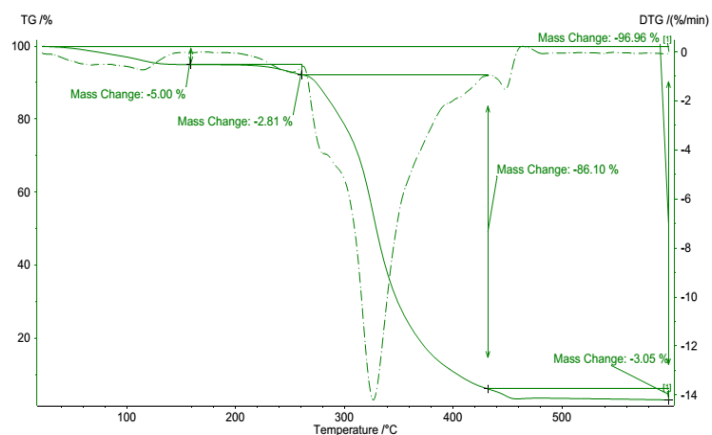


Figure 3. TGA spectra of PU3**Table 1.** Spectra data, elemental analysis of polyurethanes

Substrate	IR (KBr, cm ⁻¹)	¹ HNMR (DMSO-d ₆ , δ, ppm)	Elemental analysis					
			Calc. C	Calc. H	Calc. N	Found C	Found H	Found N
PU1	3200, 3328(NH), 3060(CH-Aro), 2944, 2864(C-H, aliph.), 1657-1712 (C=O), 1480, 11596(C=C), 1541(C-N, N-H) 3300(NH), 3050, 2950(C-H, Arom., Aliph.), 1650-1722(C=O), 1492-1660(C=C), 1533(C-N)	-	57.73	5.93	14.97	57.63	6.78	13.5
PU2	3312(NH), 3090, 2944(C-H, Arom., Aliph.), 1600-1720(C=O), 1486-1600(C=C), 1542(C-Nn N-H)	9(NH), 7-8.1(phenyl), 4.5 (methylene), 2.1(methyl).	59.98	4.24	14.74	59.63	5.0	13.5
PU3	3312(NH), 3090, 2944(C-H, Arom., Aliph.), 1600-1720(C=O), 1486-1600(C=C), 1542(C-Nn N-H)	7.1(NH), 7.8-8.2(phenyl), 4.4(methylene), 2.7-3(C-H, CH ₂), 0.8-1.5(methyl).	61.65	6.59	13.08	61.5	7.96	11.7 4

Table 2. Solubility of polyurethanes.

Polym. code	NMP	DMF	DMSO	TCE	THF	H ₂ SO ₄	HMPA	N,N-DMAC	Aceton	Ethanol	Methanol	CHCl ₃
PU1	+	+	+	-	-	+	±	+	-	-	-	-
PU2	+	+	+	-	-	+	±	+	-	-	-	-
PU3	+	+	+	-	-	+	+	+	-	-	-	-

Soluble (+), partially soluble (±), insoluble (-)

Solubility tested with 0.5 g of polymer in 100 mL of solvent.

NMP=N-methylpyrrolidone, DMF=dimethylformamide, DMSO=dimethylsulfoxide,

TCE=tetrachloroethane, Py=pyridine, THF=tetrahydrofurane

HMPA=hexamethylenphosphoramide, DMAC=dimethylacetamide

Table 3. Thermal analysis, viscosity and yield of the polyamides.

Compound code	T _{5%} (°C) ^a	T _{10%} (°C) ^b	T _{50%} (°C) ^c	%Ch. Y. ^d	η _{inh} (dl/g) ^e	MW
PU1	263	285	350	8	0.55	55000
PU2	245	263	355	20	0.6	60000
PU3	245	275	330	3	0.5	50000

^a 10% weight loss^b 10% weight loss^c 50% weight loss^d Char yield percent at 600 °C, obtained from TGA.^e Measured in DMF at 25 °C (c=0.5 g/dl).

Results and Discussion

Synthesis of Monomer

2,3-bis(2-hydroxy ethyl)-2,3-dihydro-1,4-phthalazinedione was synthesized from the reaction (reflux) of phthal hydrazide with 2-equivalan-bromoethanol in *N, N*-dimethylacetamide solvent for 48 h (Scheme 2). The melting point was 132–134 °C. These regions of the IR spectra were of particular interest, the IR (KBr): ν 3200(O-H), 3090, 2850, 1660 (C=O), 1590, 1550, 1490, 1445, 1420, 1332, 1289, 1165, 1143, 1087, 1045 (C-O), 900, 798, 758 cm⁻¹. ¹HNMR data with ¹HNMR (DMSO), the ¹HNMR (500 MHz, DMSO-d₆): δ 8.1 (m, 4H, ArH), 4.9 (m, 1H, OH), 4.1 (m, 8H, CH₂).

Synthesis of Polyurethanes PU1, PU2, PU3

The polyurethane (PU1), were prepared which is given in Scheme 3. IR, ¹HNMR and elemental analysis data for the PU1 of the present study was found to be in good agreement with the results of calculated method. The results of elemental analysis are presented in Table 1. These regions of the IR spectra are of particular interest, the IR (KBr), ν 3200, 3328(NH), 3060(CH-Aro), 2944, 2864(C-H, aliph.), 1657-1712 (C=O), 1480, 11596(C=C), 1541(C-N, N-H) cm⁻¹.

¹HNMR and elemental analysis data for the PU2 of the present study is in good agreement with the results. These regions of the IR spectra are of particular interest, the IR (KBr): ν 3300 (N-H),

3050, 2950, 1722(C=O), 165(C=O), 1600, 1533, 1443, 1330, 1220, 1100, 780 cm⁻¹. The NMR data with ¹HNMR (DMSO), ¹H-NMR, (500 MHz, DMSO-d₆): δ 9.6 (br, NH), 7-8.1 (m, 7H, ArH), 4.5 (m, 4H, CH₂), 2.1 (t, 3H, CH₃). The elemental analysis data for the PU3 of the present study is in good agreement with the results. The results of the elemental analysis are presented in Table 1. The regions of the IR spectra are of particular interest, the IR (KBr): ν 3312 (N-H), 3090, 2944, 1720 (C=O), 1643 (C=O), 1585, 1542, 1486, 1458, 1330, 1239, 1128, 780, 737, 695 (cm⁻¹) and NMR data with ¹HNMR (DMSO): ¹H-NMR, (500 MHz, DMSO-d₆): δ 7.8-8.2 (m, 4H, ArH), 7.1 (br, 1H, NH), 4.4(m, 4H, CH₂), 2.7 (t, 2H, CH₂), 3 (d, 1H, CH), 0.8-1.5 (m, 15H, 3CH₃, 3CH₂). CH₂), 2.1 (t, 3H, CH₃).

One of the major objectives of this study was to produce Polyurethanes with improved solubility. The solubility of these Polyurethanes was determined for the powdery samples, and the results are listed in Table 2. All PURs were readily soluble in common polar aprotic solvents without need for heating (except: THF). Also, by heating they were soluble in a less efficient solvent such as THF. Among these polymers, the polyurethane PU3 was more soluble in common solvents, and shorter time was needed for complete dissolution.

The limiting viscosity number [η] of polyurethane was determined for extracted and dried polymers in DMF, depending on the solubility of the polyurethane. For the same or similar type of linear polymers the [η] value was

proportional to the molecular mass. The inherent viscosities of the PU1 and PU2 and PU3 obtained in DMF were at the range of 0.5-0.6 dl/g that revealed reasonable molecular weights. Thermal stability of the polyurethanes was also evaluated using TGA technique. Temperatures of the 50% weight loss and the remained polyurethanes at 600 °C in nitrogen atmosphere are tabulated in Table 3. The representative TGA curves are demonstrated in Figures 1, 2 and 3. All the polymers were stable up to 200 °C in nitrogen and showed relatively the same stability. We found that these polyurethanes did not reveal obvious weight loses until the temperature reached 200 °C in nitrogen, implying that no thermal decomposition occurred. The 50% weight loss of all polymers was in temperature range of 330 °C. The polyurethane (PU1) remained 8% of the original weight at 600 °C in nitrogen and the polyurethane (PU2) remained over 20% of the original weight at 600 °C in nitrogen and the polyurethane (PU3) remained over 3% of the original weight at 600 °C in nitrogen.

Conclusion

Combination of 2,3-bis (2-hydroxy ethyl)-2,3-dihydro-1,4-phthalazinedione has recently attracted a great deal of attention from chemists and pharmacists due to its remarkable medicinal properties. In this research study, 2,3-dihydro-1,4-phthalazinedione and its derivative 2,3-bis(2-hydroxy ethyl)-2,3-dihydro-1,4-phthalazinedione were used in the preparation of new polymeric compounds. In addition the favorable polymer properties such as viscosity and high thermal resistance, due to the presence of the phthalazine nucleus in the structure of these polymers, we can expect medicinal properties for these polymers. Comparison of the thermal analysis (TGA) of the obtained polymers showed a better thermal stability of the polyurethane obtained

from toluene diisocyanate with 20% residual mass compared with that of the other polymers.

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Compliance with ethical standards

The authors declare that they have no conflict of interest.

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