

Synthesis of new polyurethanes based on 5, 6, 7, 8 – tetrabromo – 2, 3 – dihydro – 1, 4 – phthalazine dione**Ommolbanin Gharib^a, Hossein Nasr-Isfahani^a, Mohammad Bakherad^a, Hossein Mighani^{b,*}**^aCollege of Chemistry, Shahrood University of Technology, 3619995161, Shahrood, Iran^bFaculty of Science, Department of Chemistry, Golestan University, P.O. BOX 155, Gorgan, Iran

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Abstract

In this work, 5,6,7,8-Tetrabromo-2,3-dihydro-2,3-bis(2-hydroxyethyl)phthalazine-1,4-dione is synthesized by the reaction of 5,6,7,8-tetrabromo-2,3-dihydrophthalazine-1,4-dione with 2-bromoethanol in the presence of triethylamine. The obtained monomer was polymerized with different diisocyanates, including hexamethylenediisocyanate (HMDI), tolylene-2,4-diisocyanate (TDI), isophoronediiisocyanate (IPDI), 1,4-phenylene diisocyanate (*p*-PDI) and 4,4'-methylenebis (phenyl isocyanate) (MDI), to obtain polyurethanes. The measured viscosity for these polymers is in the range of 0.5-0.6 dl·g⁻¹. The structure of the synthesized polymers was analyzed by infrared (IR), ¹H-NMR spectroscopy methods, viscometry measurements, thermal gravimetric analysis (TGA/DTG), as well as elemental analysis. All the polyurethanes showed very good solubility in common aprotic polar solvents. The good solubility of the polyurethanes can be due to presence of bulky pendant group as side group. The inherent viscosity of the polyurethanes in the range of 0.5 – 0.6 dL/g indicated the relatively high molecular weight. The diol synthesized here is reported for the first time, and data from different spectra analyses were used to confirm the structures of all compounds. 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.

Keywords: Diol; polyurethanes; inherent viscosity; solubility; IR-spectroscopy; ¹HNMR-spectroscopy; thermal gravimetric analysis.

Introduction

The discovery of polyurethane was made by Bayer and colleagues in 1937 [1]. Polyurethanes are a group of elastomeric polymers [2] that form the most diverse family of polymeric materials [3] and are formed by the increasing reaction between the

isocyanate functional groups [3] and the hydroxyl agent [4]. As an example, polyurethane [5] can be obtained from the increasing reaction between hexamethylenediisocyanate [6] and polyethylene glycol [7,8]. The diisocyanates can be either aromatic or aliphatic and generally aromatic

*Corresponding author: Hossein Mighani

Tel: +98 (911) 9112730284, Fax: N/A

E-mail: hmighani@gmail.com

isocyanate such as methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) have a higher reactivity compared to the aliphatic isocyanates like hexamethylene diisocyanate (HMDI). Recently, bio-based diisocyanates such as penta-methylene diisocyanate (PDI) have been commercialized to enable 100% bio-based polyurethanes [9]. Polyurethane chains are composed of two flexible segments (soft section) and a relatively rigid section (hard section) [10]. The hard section of polyurethanes is composed of urethane groups formed by the reaction of diisocyanate with short-chain diols, while the flexible soft section is composed of long-chain polyethylene diols with a molecular weight of 500 to 5000 polyols [11]. The synthesis path and the ratios of these two fractions determine the mechanical properties of the polymer such as its tensile properties, crystallization temperature, and melting point [12]. Various parameters such as DL chain length, diisocyanate space chemistry, and used catalyst are effective in determining the ratio of the hard and the soft segments [13]. Over the last century, technological advances have led to the use of materials that are fire-resistant [14]. Bromine is an important element in seawater, lake salt, and earth's crust [15]. Salts and compounds have important applications in photography, and also in the pharmaceutical industry [14]. Halogenated organic compounds such as tetrabromophthalic anhydride [14] are flame retardants [16]. The chemical structure, high molecular weight, and chemical bond strength in tetra-bromophthalic anhydride leads to flame retardation properties [17]. Tetrabromophthalic anhydride has an important role in the manufacture of fire-resistant polyesters and epoxy

resins [18], plastics, and textiles, as well as hard polyurethane foams [19].

The recent work has demonstrated that hydroxyalkylation can be prepared by using cyclic carbonates such as propylene carbonate [20,21]. As an example of lignin functionalization, propylene carbonate has been used to obtain a hydroxypropylate phenolic hydroxyl groups that are proposed to esterify by non-aromatic alcohols [22]. Nitrogen-containing heterocyclic compounds have an important application in the manufacture of biologically active compounds, pharmaceuticals, and chemicals [23]. These compounds are widely needed in nature and life [24]. Heterocyclic compounds containing polysaccharide hydrazine are one of the most interesting ones among the different types of nitrogenated organic compounds due to their clinical and medicinal properties [25]. The discovery of the first naturally occurred pyridazine derivative (pyridazomycin) provided an essential step in the recognition of the 1 and 2 diazine nuclei, which is a valuable nucleus in pharmaceutical chemistry [26]. 1-Arylamino-2 and 3-dihydro-H1-pyrazole [1,2- b] phthalazine-5, 10-dione is a phthalichydrazide derivative that has anti-inflammatory, analgesic, and antipyretic properties [27]. Hydralazine, a derivative of phthalichydrazide, has a wide application as a vasodilator and antihypertensive [28]. Tetrabromophthalohydrazide (8, 7, 7, 5, 5-tetrabromo-3, 2-dihydro-phthalazine dione) is a two-functional, heterocyclic, nucleophilic compound [29] that contains two relatively acidic protons (ability to react with two-functional compounds) [30].

In this article, tetrabromophthalichydrazide were

utilized in the preparation of new polymeric compounds. The novelty of the research is that the diol was synthesized for the first time, while the data from spectra were used to confirm the structures of all compounds. The result shows that new material has been correctly synthesized. It is worth mentioning that these polymers, in addition to having favorable properties such as viscosity and high thermal resistance, have also expected medicinal properties due to the presence of phthalazine nucleus in their structure.

Experimental

Materials and instruments

All materials and reagents as well as solvents were purchased from Fluka (Switzerland) and Merck (Germany) and used without purification. ¹HNMR spectra were recorded on a 500 MHz Bruker Advance DRX instrument

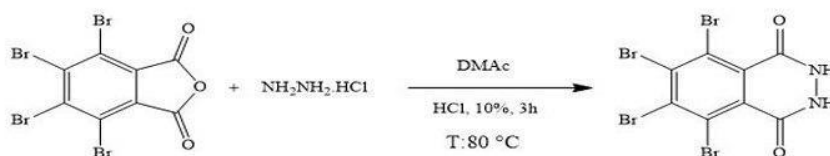
(USA) using DMSO-d₆ as solvent and tetramethylsilane as an internal standard. FTIR spectra were recorded using a Bruker Vector 22 spectrometer (USA) on KBr pellets. The CHN- 600 Leco analyzer (Germany) was used for elemental analysis and Thermal gravimetric analysis (TGA) (IPPI). Inherent viscosity ($\eta_{inh} = L\eta_{rel}/C$) of polymers was determined for a solution of 0.5 g/dl in NMP at 25 °C using an Ubbelohde viscometer.

Preparation of monomers

Synthesis of 5, 6, 7, 8- tetrabromo-2, 3-dihydro- 1, 4-phthalazinedione (tetrabromophthalhydazide)

This compound was synthesized from the reaction of tetra-bromophthalic anhydride with hydrazine hydrate in dimethyl acetamide solvent (Scheme 1.).

IR(cm⁻¹): 3288(NH), 1622(C=O), 1600, 1450(C=C Aro.), 660(C-Br).



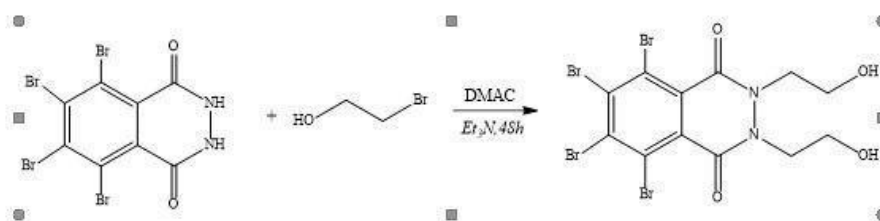
Scheme 1. Synthesis of 5, 6, 7, 8- tetrabromo-2, 3-bis(2-hydroxyethyl)-2, 3-dihydro- 1, 4-phthalazinedione

This compound was synthesized from the reaction (reflux) of tetra-bromophthalic anhydride with 2-bromoethanol in dimethyl acetamide solvent within 48 hours (Scheme 2).

IR(KBr): 3425, 3296, 2931, 1722,

1371, 1334, 1269, 1157, 1068, 922, 741, 658 cm⁻¹

¹³C-NMR,(80 MHz, DMSO-d₆): 57.1, 59.7 (CH₂), 120.8, 130.1, 136.7 (Ar), 163.1 (C=O)

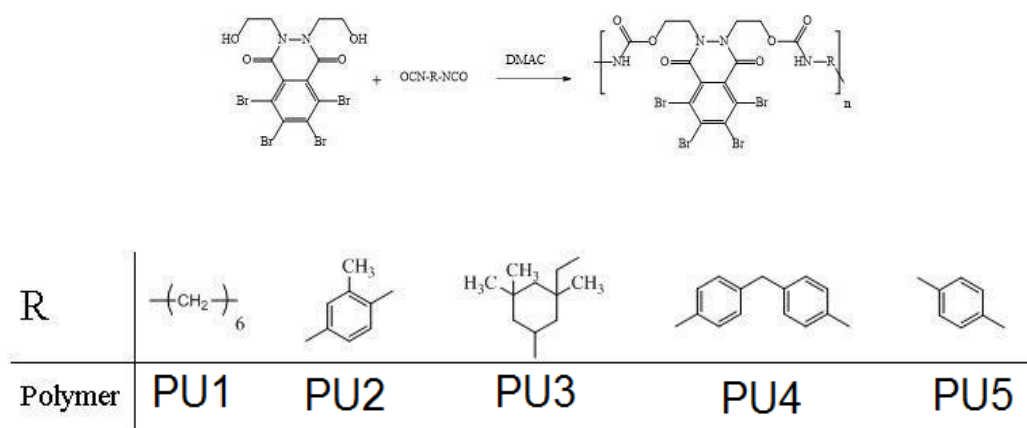


Scheme 2

Preparation of polyurethanes

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

toloylenediisocyanate, isofurenediisocyanate, methylenediphenyldiisocyanate, and 1,4 -phenylenediisocyanate with an equal molar amount in dimethyl acetamide solvent (Scheme 3).



Scheme 3

Table 1. Spectra data, elemental analysis results of polyurethanes

Substrate	IR (KBr, cm ⁻¹)	¹ HNMR (DMSO-d ₆ , δ, ppm)	Elemental analysis					
			Calc.			Found		
			C	H	N	C	H	N
PU1	3368(NH), 2864(C-H, aliph.),1776, 1727 (C=O)	5.7(H, NH), 3.4- 1.5(H, aliph.).	32.88	3.01	7.67	32.02	2.52	7.43
PU2	3300(NH), 2925(C-H, Aliph.),	8.1(NH), 6.5(phenyl), 3.2(methylene),	59.26	5.05	17.28	59.45	4.95	17.18

	1727(C=O), 1450(C=C), 1221-1163(C-O)	1660- 1531(C-N),	2.3(methyl).									
PU3	3300(NH), 2921(C-H, Arom.,Aliph.), 1728(C=O), 1237-1131(C-O), 663(C-Br).	2951, 1777-	5.6(NH), 3.1(methylene), 0.8(methyl).	3.8- 1.5-	59.77	5.75	16.09	59.42	5.82		16.02	
PU4	3300(NH), 2923(C-H, Arom.,Aliph.), 1727(C=O).	3100, 1777-	8.7(NH), 7(methlenediphenyl), 4.1-3.2(methylene), 3.7(CH ₂ -methylene diphenyl).	7.4-	56.67	3.49	20.12	56.48	3.82		20.14	
PA5	3300(NH), 2952(C-H, Aliph.), 1726(C=O), 1124(C-O, uethe)	3100, Arom., 1777- 1128-	8.5(NH), 4.1-3(methylene).	7.8(Arom.),	64.05	3.91	14.94	63.94	4.12		14.78	

Table 2. Solubility of polyurethanes

Polym. code	NMP	DMF	DMSO	TCE	THF	H ₂ SO ₄	HMPA	DMAC	Aceton	Ethanol	Methanol	CHCl ₃
PU1	+	+	+	-	-	+	±	+	-	-	-	-
PU2	+	+	+	-	-	+	±	+	-	-	-	-
PU3	+	+	+	-	-	+	+	+	-	-	-	-
PU4	+	+	+	-	-	+	±	+	-	-	-	-
PU5	+	+	+	-	-	+	±	+	-	-	-	-

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

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

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

TCE=tetrachloroethane, Py=pyridine, THF=tetrahydrofurane

HMPA=hexamethylenphosphoramidate, DMAC=dimethylacetamide

Table 3. Thermal analysis, viscosity, and char yield of the polyurethanes

Compound code	T _{5%} (°C) ^a	T _{10%} (°C) ^b	T _{50%} (°C) ^c	%Ch. Y. ^d	η _{inh} (dl/g) ^e	MW
PU1	252	290	415	20	0.53	53000
PU2	220	265	420	39	0.5	50000
PU3	230	270	340	25	0.5	50000
PU4	210	270	450	40	0.6	60000
PU5	225	250	420	35	0.53	53000

^a10% weight loss, ^b10% weight loss, ^c50% weight loss, ^dChar 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 and polymers

This compound was synthesized by the reaction (under reflux) of tetrabromophthalic anhydride with 2-bromoethanol in dimethyl acetamide solvent within 48 hours (Scheme 2). The melting point determined to be 134 – 136 °C. These regions of the IR

spectra in Figure 1 are of particular interest, the IR(KBr): 3425, 3296, 2931, 1722, 1371, 1334, 1269, 1157, 1068, 922, 741, 658 cm⁻¹ and NMR data in Figure 2 as ¹³C-NMR (DMSO): δ(ppm) ¹³C-NMR,(80 MHz, DMSO-d₆): 57.1, 59.7 (CH₂), 120.8, 130.1, 136.7 (Ar), 163.1 (C=O).

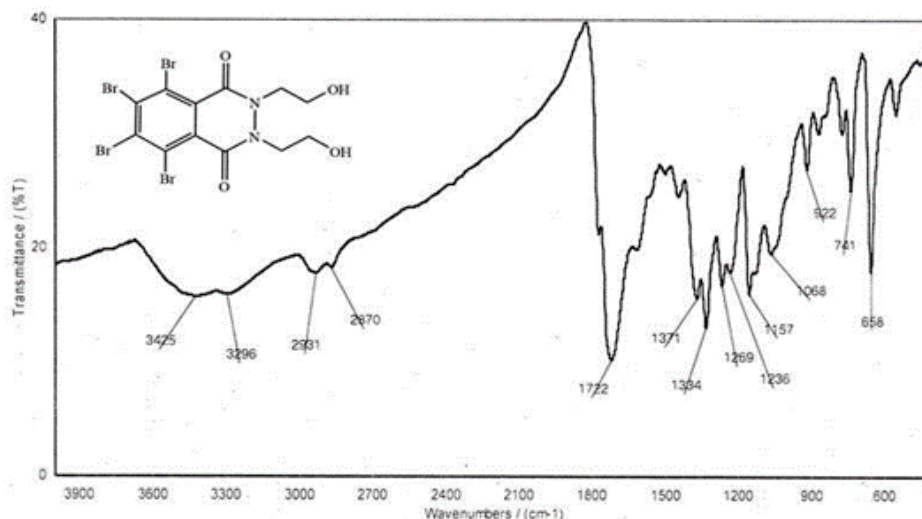


Figure 1. FTIR spectra of dione

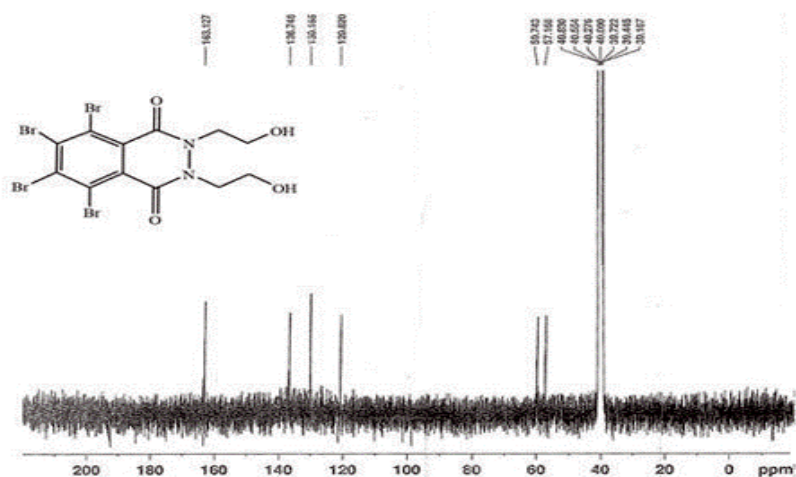


Figure 2. ^{13}C NMR spectra of dione

Polyurethanes PU1, PU5

The polyurethane (PU1) was prepared according to the procedures which are given in Scheme 3. IR, ^1H NMR, and elemental analysis data for the PU1 of the present study are in good agreement (Figure 5). The results of elemental analysis are given in Table 1. These

regions of the IR spectra in Figure 3 are of particular interest, the 3368 cm^{-1} (NH) and, 2925 , 2864 (C-H, Aliph.), 1776 , 1727 (C=O) and NMR data in Figure 4 as ^1H NMR (DMSO): δ (ppm) 5.7 (H, N-H), 3.4 (H-Aliph, N-H), 1.5 (H-Aliph).

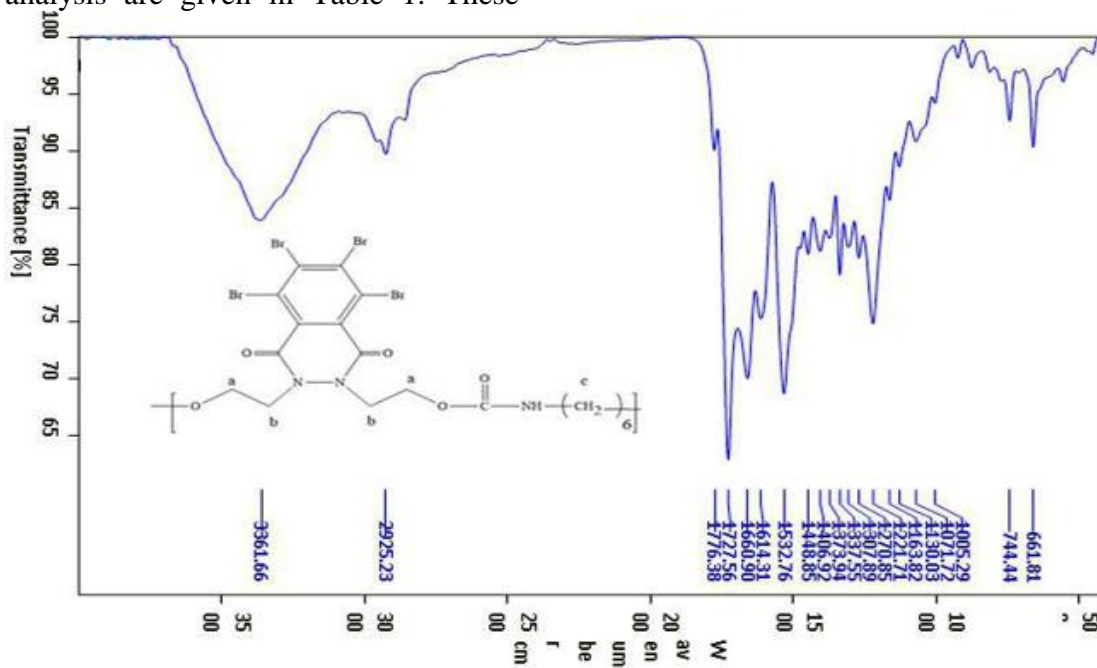


Figure 3. FTIR spectra of PU1

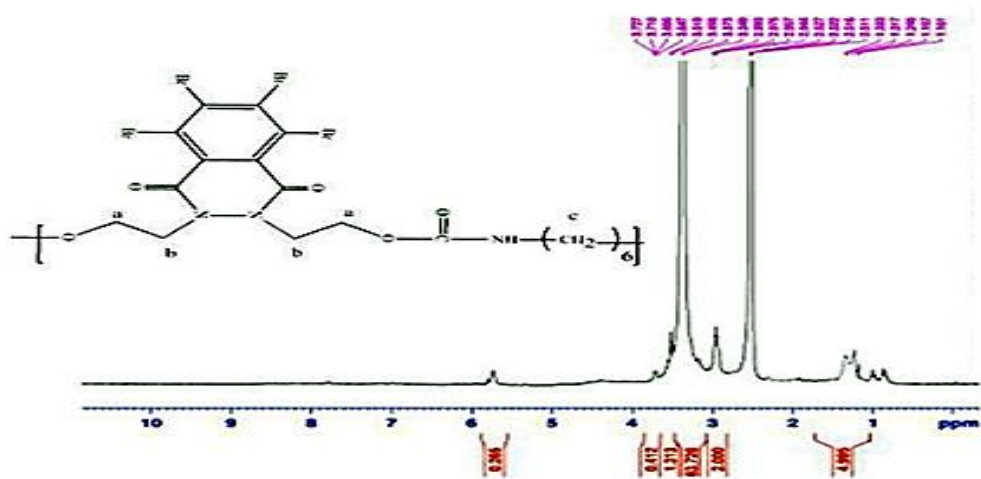


Figure 4. ¹H NMR spectra of PU1

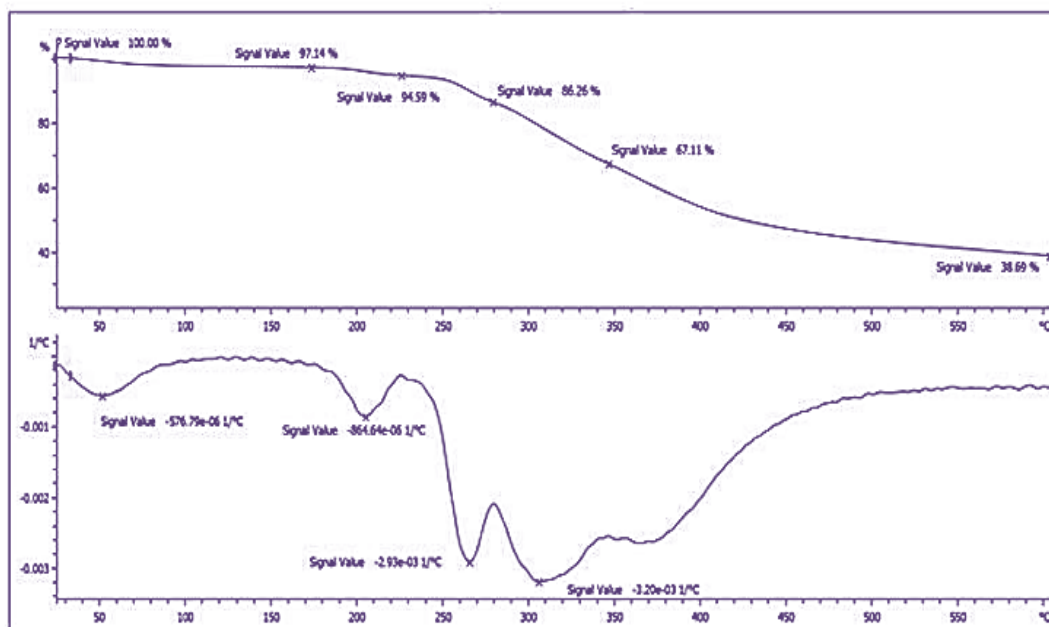


Figure 5. TGA spectra of PU1

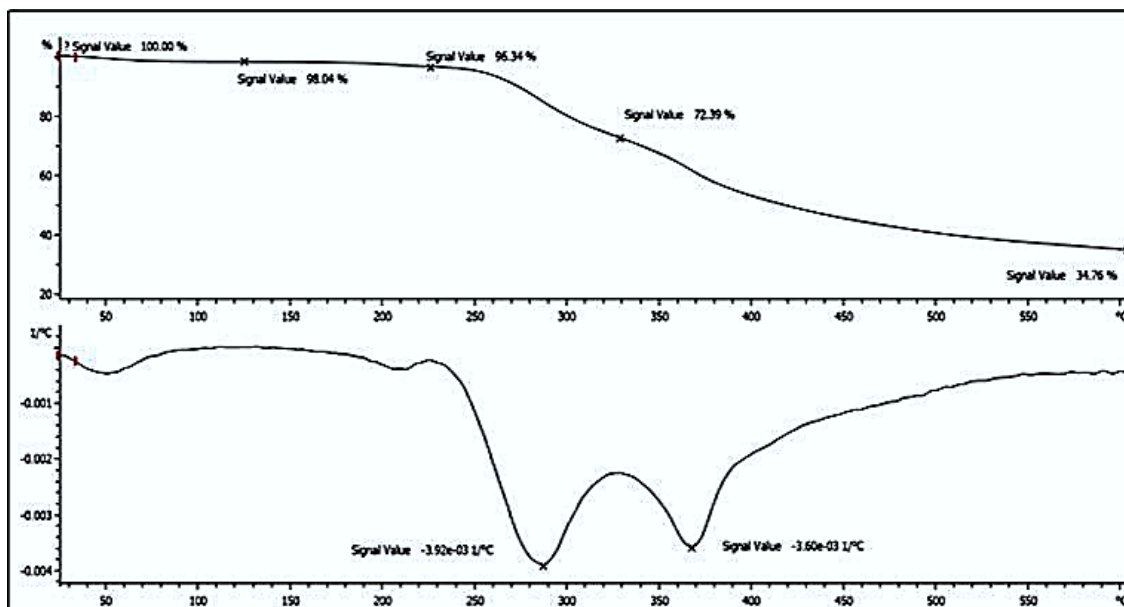


Figure 8. TGA spectra of PU5

The solubility of polyurethanes were tested in different organic solvents at room temperature and the results are shown in Table 2. All the polyurethanes showed very good solubility in common aprotic polar solvents such as NMP, DMF, DMSO, and DMAc. The good solubility of the polyurethanes can be due to the presence of bulky pendant group as side group. The limiting viscosity number $[\eta]$ 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 $[\eta]$ value is proportional to the molecular mass. The inherent viscosities of PU1 and PU5 obtained in DMF were in the range of 0.5 – 0.6 dl/g that revealed a reasonable molecular weight. The inherent viscosity of the polyurethanes in the range of 0.5 – 0.6 dL/g indicated the relatively high molecular weight. These numbers of the inherent viscosity for polyurethanes indicate the molecular mass suitable for such polymers. The thermal stability of all polyurethanes was also evaluated by TGA. The

temperatures of the 50% weight loss and the remained polyurethanes at 600 °C in nitrogen atmosphere were given in Table 3. The representative TGA curves are shown in Figures 5 and 8. All the polymers were stable up to 200 °C in nitrogen and showed almost the same stability for all samples. We found that these polyurethanes did not show apparent weight losses until the temperature reached 200 °C under nitrogen, implying that no thermal decomposition occurred. The 50% weight loss of all polymers was in the temperature of about 340 °C. The 20% of the original weight of the PU1 and over 35% of the original weight of the PU5 remained at 600 °C under nitrogen.

Conclusion

The combination of tetra-bromo-tetrahydrazide (5, 6, 7, 8-tetra-bromo-2, 3-dihydro-1, 4-phthalazinedione) has recently attracted the attention of chemists and pharmacists due to its remarkable medicinal properties. In this study, tetrabromophthalichydrazide and the derivative (5, 6, 7, 8-tetrabromo-2, 3-bis (2-hydroxyethyl) -

2,3-dihydro-1,4-phthalazin dione) were used to prepare new polymeric compounds which, in addition to having desirable polymer properties such as viscosity and high thermal resistance, have also potential medical applications due to the presence of phthalazine nucleus in their structure. All the polyurethanes showed very good solubility in common aprotic polar solvents. The good solubility of the polyurethanes can be due to the presence of bulky pendant group as side group. The inherent viscosity of the polyurethanes in the range of 0.5 – 0.6 dL/g indicated the relatively high molecular weight. A comparison of the thermal analysis (TGA) of the obtained polymers showed better thermal stability of the polyurethane obtained from the toluene diisocyanate compared to the other polymers. PU adhesives can possess some of the best performance characteristics of all adhesives, and they are particularly important in the production of engineered wood products (e.g., cross-laminated timber) as a binder. They are colorless and moderately flexible and can be used for bonding wood, metal, glass, plastic, rubber, ceramic, sand, and textile fiber and these adhesives can be made using compounds such as phthalazindione.

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