Turkish Journal of Chemistry

Volume 32 | Number 3 Article 8

1-1-2008

Synthesis and Characterization of Novel Polyamide and Polyhydrazides Based on the 6,6´-disubstituted-2,2´-bipyridine

ABDURRAHMAN ŞENGÜL

HÜLYA ARSLAN

Follow this and additional works at: https://journals.tubitak.gov.tr/chem

 Part of the Chemistry Commons

Recommended Citation

ŞENGÜL, ABDURRAHMAN and ARSLAN, HÜLYA (2008) "Synthesis and Characterization of Novel Polyamide and Polyhydrazides Based on the 6,6´-disubstituted-2,2´-bipyridine," *Turkish Journal of Chemistry*: Vol. 32: No. 3, Article 8. Available at: https://journals.tubitak.gov.tr/chem/vol32/iss3/8

This Article is brought to you for free and open access by TÜBİTAK Academic Journals. It has been accepted for inclusion in Turkish Journal of Chemistry by an authorized editor of TÜBİTAK Academic Journals. For more information, please contact academic.publications@tubitak.gov.tr.

Turk J Chem
32 (2008) , 355 – 364.
© TÜBİTAK

Synthesis and Characterization of Novel Polyamide and Polyhydrazides Based on the 6,6′-disubstituted-2,2′-bipyridine

Abdurrahman ŞENGÜL* **and Hülya ARSLAN**
Department of Chemistry, Faculty of Arts and Sciences, Karaelmas University, 67100 Zonguldak-TURKEY
e-mail: abdurrahmans2002@yahoo.co.uk

Received 26.10.2007

The monomers namely 6,6′-dicarbonylchloride-2,2′-bipyridine (**1**) and 6,6′-dihydrazine-2,2′-bipyridine (**2**) were synthesized and characterized thoroughly. The polyhydrazides (**PHZ1** and **PHZ2)** were obtained by direct polycondensation of **2** with terephtaloylchloride (**TPCl**), and novel polyamide (**PA1**) by direct polycondensation of **1** with hexametyhlenediamine (**HMDA**). Polymers with low PDIs were generated in all cases (PD $\sim$ 1.02-1.3). The polymers were characterized by ^{1}H and ^{13}C NMR, FT-IR, and Gel Permission Chromatography (GPC).

Key Words: Bipyridine, polyamide, hydrazide, polymer, terephtaloylchloride.

Introduction

Research in the syntheses of rigid rod aromatic polyamides containing polypyridine moieties has been a very interesting area because of their unique and specific photophysical properties and their potential applications such as polymer-supported electrodes, photosensitizers, emission sensitizers, photogalvanic cells, and metal ion sensing.[1] These rigid rod polymers have also attracted considerable interest because of their ability to form a liquid crystalline (LC) phase and their potential application as high modules and high performance thermoplastics.[2] Two series of polyamides and polyesters derived from 2,2′-bipyridine-5,5′-dicarboxylic acid have been reported.[1] It was found that these polymers exhibited modest thermal stability and can form a lyotropic liquid crystal phase above the critical concentration. In addition, the bipyridine moiety in the polymer main chain is able to form a complex with different transition metal ions. Therefore, the optical as well as the electronic properties can be manifested by the formation of metal complexes. It was shown that the complex formation brought about the enhancement of the optic properties and also the photosensitivity in the presence of photosensitive metal ions.

*Corresponding author

Recently, a series of new aromatic oligoamides based on 1,10-phenanthroline diacid and *o*-phenylenediamine have been synthesized.[3] These oligomers were found to fold into well-defined helical structures in solution through intramolecular hydrogen bonds and aromatic stacking. The helical foldamers formed in the solid state characterized by X-ray diffraction may promote the aromatic oligoamide-based helical foldamers for potential applications in biology and material science.

Wholly aromatic poly(amide-hydrazie)s exhibit some interesting and potentially useful characteristics that have enormous technical and economic importance.[4] These polymers are classified under a category of heat resistance materials.[5,6] The reasons responsible for such stability of these polymers are expected to originate primarily from their chemical structure, which is composed of building units generally known to be highly resistant to increased temperatures, such as amide groups and aromatic moieties, and also expected to be due to their considerable crystallinity, which should be promoted by strong hydrogen bonding between the amide groups of the neighboring chain segments.[7]

The inherent ability of bipyridine, polyamides, and polyhyrazides to react with transition metal cations to form stable complexes[8−11] suggested that these polymers should be very effective complexing agents of great interest in the metallosupramolecular chemistry. Furthermore, the polyamides possessing a coordination site have been used as supports for immobilized catalysts.[12,13] In addition, bipyridine containing aromatic polyamides were synthesized and investigated as new devices for solar energy conversion.[14]

Herein we report the synthesis and characterization of new aromatic polyamide, poly(hexamethylene-2,2′-bipyridyl amide), **PA1,** and polyhydrazides; poly(terephtaloyl-2,2′-bipyridyl hydrazide), **PHZ1** and **PHZ2**, respectively.

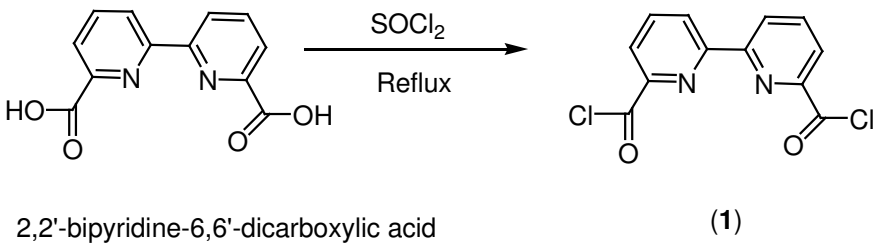
Experimental

Chemicals

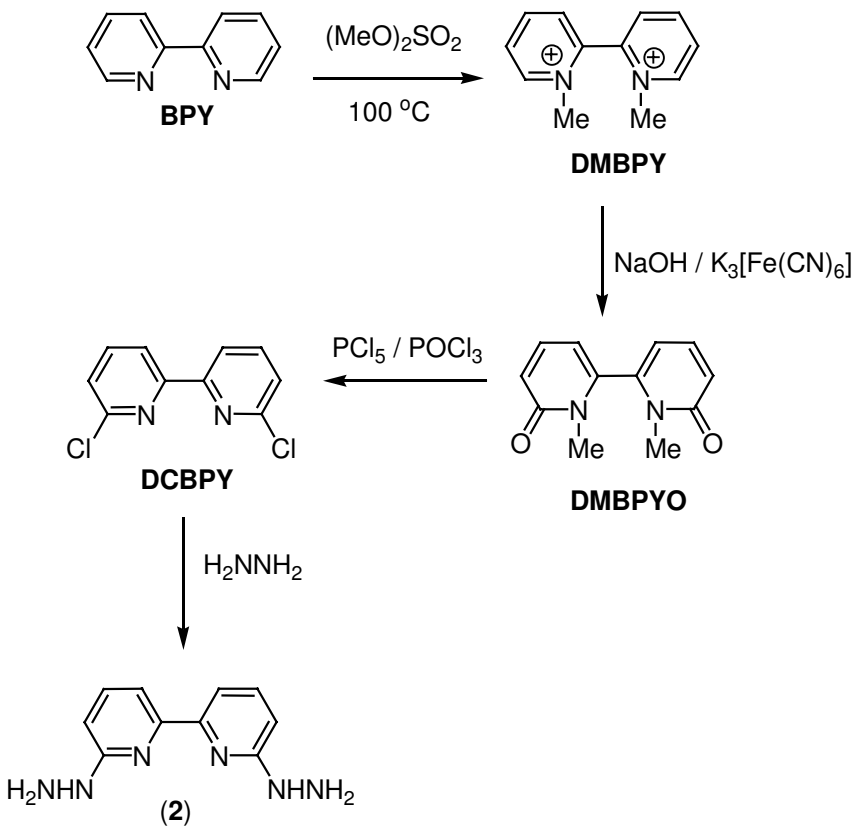
All chemicals were of reagent grade and used as received unless otherwise indicated. The precursor 2,2′-bipyridyl-6,6′-dicarbonyl chloride (**1**) was prepared according to the published procedure as shown in Scheme 1.[1] The precursor ligand 6,6′-dichloro-2,2′-bipyridine[15] was synthesized according to Scheme 2.

Synthesis of DMBPY

The mixture of 2,2′-bipyridine (**BPY**) (20.0g) and dimethylsulphate (70 mL) was set to reflux for 1 h. The solution was cooled down to room temperature, and added anhydrous diethyl ether (200 mL) with vigorous stirring. The obtained white precipitate was used for the next step without characterization.



Scheme 1. The synthesis route to 6,6′-dicarbonyl-2,2′-bipyridine (**1**).



Scheme 2. The synthesis route to 6,6′-dihydrazine-2,2′-bipyridine (**2**).

Synthesis of DMBPYO

The crude product of **DMBPY** was dissolved in 500 mL of water. To this solution, solutions of $K_3[Fe(CN)_6$ (120.0 g in 500 mL of water) and NaOH (150.0 g in 500 mL of water) were added simultaneously at 5 °C. The pH of the solution was adjusted to 8-9 by dropwise addition of HCl while cooling the solution. The solution was extracted with chloroform for several times and the combined organic phases were filtered over dry sodium sulphate. Evaporation of the solution under vacuum gave a white solid that was crystallized from benzene. M.p.: 211 °C. IR (KBr): 1650 (CO) cm-1. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 3.3 (s, 6H, NCH_3), 6.2 (dd, $^3J_{H3,H4}$ = 6.6 Hz and $^4J_{H3,H5}$ = 1.2 Hz, 2H, bpy-H3,3′), 6.7 (dd, $^3J_{H5,H4}$ = 9.0 Hz and $^4J_{H3,H5}$ = 1.2 Hz, 2H, bpy-H5,5′), 7.4 (dd, $^3J_{H3,H4}$ = 6.6 Hz and $^4J_{H4,H5}$ = 9.0 Hz, 2H, bpy-H4,4′).

Synthesis of DCBPY

To the diketone, **DMBPYO** (7.0 g) was added PCl_5 (15.0 g) and $POCl_3$ (140 mL) and set to reflux for 20 h. The excess of $POCl_3$ was removed under vacuum, and an ice-water mixture was added, making alkaline with an ammonia solution. The obtained white precipitate was recrystallized from benzene to yield colorless needle shaped crystals. M.p.: 220 °C. $C_{10}H_6N_2Cl_2$ (225.1): calc. C 53.4, H 2.7, N 12.4; found: C 53.5, H 2.8, N 12.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.4 (d, $^3J_{H5,H4}$ = 7.7 Hz, 2H, bpy-H5,5′), 7.8 (t, $^3J_{H5,H4}$ = 7.7 Hz and $^3J_{H4,H3}$ = 7.7 Hz, 2H, bpy-H4,4′), 8.4 (d, $^3J_{H3,H4}$ = 7.7 Hz, 2H, bpy-H3,3′).

Synthesis of 6,6′-dihydrazine-2,2′-bipyridine (2)

Hydrazine monohydrate (20 mL) was added to **DCBPY** (2.0 g) and set to reflux for a week under dry nitrogen with vigorous stirring. Every 12 h, additional 10 mL of hydrazine monohydrate was added (totally 5 times). Upon cooling to room temperature a yellow precipitate was collected by suction filtration, and washed with plenty of water, methanol and diethyl ether, and dried over P_2O_5. M.p.: 208 °C. EI-MS (m/z) = 216. IR (KBr): 3325 (NH_2), 3086 (CH_{ar}), 1582 (C = N) and 1450 (C = C) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 4.2 (s, 4H, NH_2), 6.7 (dd, $^3J_{H5,H4}$ = 7.7 Hz and $^4J_{H5,H3}$ = 1.4 Hz, 2H, bpy-H5,5′), 7.4 (s, 2H, NH), 7.5-7.6 (m, 4H, bpy-H3,3′ and H4,4′).

Synthesis of polyamide, PA1

A solution of **HMDA** (0.034 g, 2.4×10^{-4} mol) in NaOH (5 mL, 5 wt%) and a solution of **1** (0.076 g, 2.7×10^{-4} mol) in CH_2Cl_2 (9.0 mL) were mixed in a round-bottom flask sealed with a plastic cap. The reaction flask was placed in a water bath at 30 °C for 72 h. After a predetermined polymerization time, the excess of solvent was evaporated under vacuum and the polymer was precipitated in petroleum ether, collected by filtration and dried under vacuum at room temperature. The reaction conditions and the GPC analyses results were summarized in Table 1 and Table 2, respectively. IR (KBR): 3340 (primer amine), 2931, 1608 (amid-I), 1535 (amid-II), 1427, 1276, 1095, 782, 617 cm^{-1}

^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.5 (d, $^3J_{H3,H4}$ = 7.1 Hz, 2H, bpy-H3,3′), 7.9 (t, $^3J_{H4,H5,H3}$ = 7.8 Hz, 2H, bpy-H4,4′), 7.7 (d, $^3J_{H5,H4}$ = 7.7 Hz, 2H, bpy-H5,5′), 3.2 (s, 4H, CH_2), 1.7 (s, 8H, CH_2).

The structure of the polymer is shown in Figure 1.

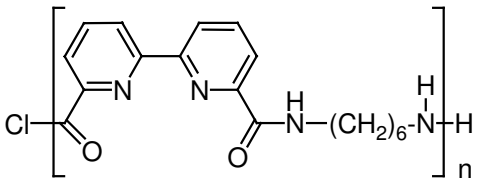


Figure 1. The idealized structure for **PA1.**

Synthesis of Polyhydrazides, PHZ1, and PHZ2

The polyhydrazides, **PHZ1,** and **PHZ2** were synthesized by condensation polymerization method by reacting **2** with **TPCl** as a condensing agent (Figure 2). 4.6×10^{-4} mol for **PHZ1** and 2.3×10^{-3} mol for **PHZ2** solutions of **2** and **TPCl** in EtOH were placed into a round-bottom flask sealed with a plastic cap (see Table 1 for stoichiometric data). To this reaction mixture, 0.06 and 0.32 mL of Et_3N were added for **PHZ1** and **PHZ2**, respectively, and the reaction mixtures were allowed to stir for 72 h at 40 °C in the case of **PHZ1,** and at 50 °C in the case of **PHZ2**. The excess of solvent was evaporated and the polymer was precipitated by adding petroleum ether. The precipitate was collected by filtration and dried under vacuum at room temperature. The initial conditions for condensation polymerization **2** with **TPCl** (Table 1) and the GPC analysis results were also given in Table 2.

IR (KBr): 3413, 3305, 3205, 3174, 3070, 2969, 2591, 1667, 1608, 1519, 1438, 1280, 1160, 110, 979, 898, 790, 597 cm^{-1} for **PHZ1**.

^{1}H NMR (400 MHz, DMSO-d$_6$, 25 °C): δ = 10.7 (s, NH), 9.2 (s, Ar), 8.1 (d, $^3J_{H3,H4}$ = 7.4 Hz, bpy-H3), 7.8 (t, ^3J = 7.8 Hz, bpy-H4), 6.9 (d, $^3J_{H5,H4}$ = 7.8 Hz, bpy-H5), 3.5 (br, s, NH_2), for **PHZ1**.

IR (KBr): 3447, 3225, 2980, 2938, 2741, 2676, 2490, 1720, 1664, 1474, 1397, 1272, 1170, 1102, 1028, 845, 805, 725 cm^{-1} for **PHZ2**.

^{1}H NMR (400 MHz, DMSO-d$_6$, 25 °C): δ = 8.1 (s, Ar), 7.6 (m, J = 7.1 Hz and 7.9 Hz, bpy-H3 and bpy-H4), 6.7 (d, $^3J_{H3,H4}$ = 7.9 Hz, 2H, bpy-H3), 4.4 and 1.3 (EtOH), 3.1 -1.2 (Et_3N) for **PHZ2.**

^{13}C NMR (400 MHz, DMSO-d$_6$, 25 °C): δ = 165.5, 161.4, 153.9, 137.9, 134.2, 129.9, 110.1, 107.3, 61.7, 45.8, 14.6, 8.9.

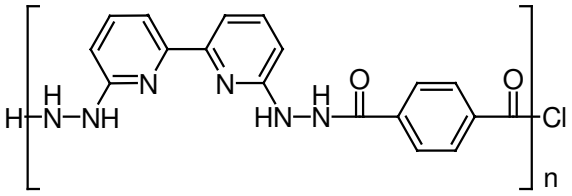


Figure 2. The idealized structure for **PHZ1** and **PHZ2**.

Table 1. Results and initial conditions for the condensation polymerization of **1** with **HMDA** and **2** with **TPCl**, respectively.

	1 mol	CH_2Cl_2 mL	HMDA mol	5% NaOH mL	**2** mol	EtOH mL	TPCl mol	EtOH mL	T °C	t h	Yield g
PA1	2.7×10^{-4}	9.0	2.4×10^{-4}	5.0	-		-		30	72	0.03
PHZ1	-		-		4.6×10^{-4}	8.0	4.6×10^{-4}	7.0	40	72	0.08
PHZ2	-		-		2.3×10^{-3}	8.0	2.3×10^{-3}	7.0	50	72	0.29

HMDA = Hexamethylenediamine, **EtOH** = Ethyl alcohol, **TPCl** = Terephthaloyl chloride.

Table 2. GPC analysis results of the polymers.

Run No	GPC		
	M_n	M_w	M.W.D
PA1	136133	139086	1.02
	730	837	1.15
PHZ1	1153039	1501937	1.30
	197157	216289	1.09
PHZ2	579	669	1.16

Results and Discussion

Monomer synthesis

6,6′-dichloro-2,2′-bipyridine was prepared starting from 2,2′-bipyridine via a three-step reaction sequence. The synthetic route is outlined in Scheme 2. The dihydrazino derivative was prepared by prolong refluxing

of the dichloro derivative with excess of hydrazine monohydrate under dry N_2 atmosphere. The structures of the intermediates were confirmed by melting points, elemental analysis, and infrared ^{1}H NMR spectrometers.

Preparation of polyamide (PA1)

All of these polymers are novel and prepared for the first time in our laboratory. All the polymers were produced in a quantitative yield. The structure of **PA1** (Figure 1) was ascertained by IR and ^{1}H NMR spectrometers. The IR spectra showed characteristic absorption near 3200-3440 cm^{-1}, ascribed to the stretching of N–H linkages with relatively strong frequency. The band at 2930 cm^{-1} is attributed to an asymmetric vibration of CH_2. The band at 1620 (C=O) is peculiar to secondary amide groups [amide-II: υ(CN) + δ(C–N–H)], and 1535-1430 cm^{-1} are attributed to C=N and C=C vibration modes. The band near at 1200-1300 can be assigned as amide-III band.[16] The band at 780 cm^{-1} is attributed to CH deformation mode, and 610 to primary amide. In the ^{1}H NMR spectra as shown in Figure 3, the absorption signals of aromatic protons appeared in the region of δ = 7.5-8.5 ppm. The corresponding NH peak is appeared at 6.6 ppm, and the aliphatic protons at 3.2-1.7 ppm. The accompanying multiplets of smaller magnitude around each main peak may correspond to defect sites and cross-linking as described by Euler[17] and Petersen[18] or due to differences in the chain conformation in the solvent which is quite common to oligomers based on bipyridine or phenanthroline ligands.[19,20] Although, the chemical shifts of the protons are consistent with the structure as expected, the integral ratio for the HMDA protons is not correct. The integral ratio for the aromatic protons include the accompanying smaller multiplets around each main peak may result anomalous ratio. The peak at 3.2 ppm may arise from impurity of the solvent used and interfere with the aliphatic proton signals. If we take the integral for one aromatic proton as 0.65, then the CH2 protons of HMDA at 1.7 ppm (integral ratio = 1.39) could correspond to 8 protons for the repeating unit of 1-HMDA-1. In that case, the methylene protons attached to nitrogen atoms should appear at 3.2 ppm with the integral ratio of 0.65. Therefore, the observed integration ratio of 4.13 may due to unrealistic integration since the integral of solvent peak is included, and also one should bear in mind that the spectrum may belong to a mixture of polymers with different molecular weights. In addition, the presence of impurity in the solvent used may not be excluded due to its extremely high integral ratio that co-exists with the expected protons.

The molecular weight of the polymer was determined by GPC analysis. The GPC chromatogram was bimodal for **PA1** because of the mixtures of polymers with M_n = 136,133 and tetramers with M_n = 730 (Table 2). The structure of tetramer can be formulated as **1-HMDA-1-HMDA** (where the calculated molecular weight of tetramer will be 245.5 + 138 + 210 + 139 = 732.5, since the molecular weight of **1** is 281 g/mol and molecular weight of **HMDA** is 140 g/mol) because of the consistency between the calculated molecular weight of tetramer and the M_n value measured by GPC.

Preparation of polyhydrazides (PHZ1) and (PHZ2)

The polyhydrazides were synthesized by direct condensation of 6,6′-dihydrazine-2,2′-bipyridyl with **TPCl** in absolute ethanol in the presence of Et_3N under N_2 atmosphere. The polymer precipitated by the addition of petroleum ether was characterized as **PHZ2**. This polymer shows rather a crystalline form as white blocks. The other one was isolated from the mother solution upon evaporation and characterized as **PHZ1**. Their reaction media and GPC analyses were summarized in Tables 1 and 2. The infrared spectra of both polymers are almost essentially the same. The IR spectrum of **PHZ2** is very well resolved compared to **PHZ1**. However, the positions of the peaks remain identical. In the IR spectrum of **PHZ1**, the presence

of absorption peaks at 3400-3200 cm^{-1} ascribed to the stretching of NH linkages, and nearby 3180 is the characteristic for the stretching vibration of NH_2. This very broad band may indicate the presence of absorption of water molecules hydrogen bonded to polymeric structure. The aromatic CH vibration is observed at 3070 cm^{-1}. The hydrazide C=O band is very intense and appears at 1660 cm^{-1}. The band at 1608 cm^{-1} ascribed to aromatic C=N stretching vibration. Whereas the characteristic and very strong band at 1520 cm^{-1} is attributed to an interaction of υ(C–N) and the δ(CNH) vibration. Likewise, a moderately strong band at 1280 cm^{-1} is characteristic for secondary amides. In addition, there is a δ(NH) wagging band at around 790 cm^{-1}. The peaks at 1160-1110 are usually characteristics for hydrazides.[16]

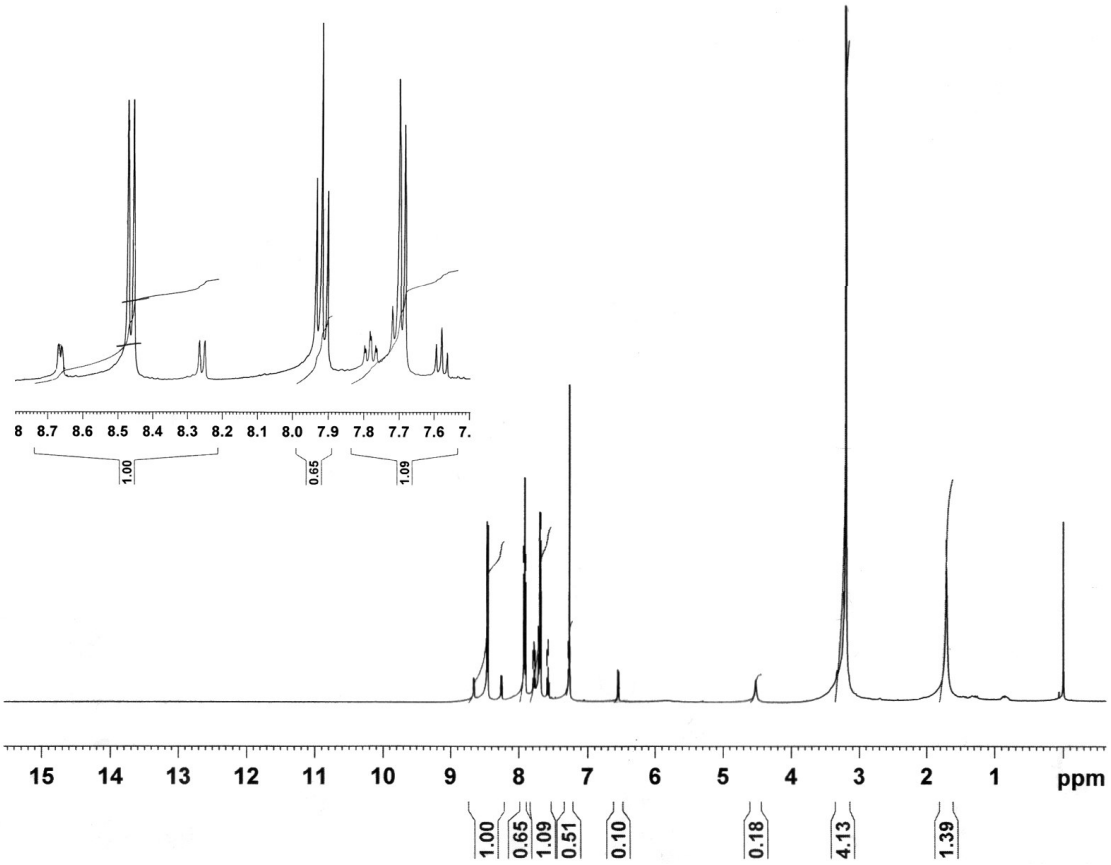


Figure 3. ^{1}H NMR spectrum of **PA1.**

The very well resolved IR spectrum of the crystalline **PHZ2** shows moderately strong and slightly broad band at 3225-3450 cm^{-1} that attributed to υ(NH) stretching vibration. The hydrazide group shows peaks at 1720-1660 cm^{-1} which is an evidence for the structure. The C=C band is observed at 1474 cm^{-1}. The strong band at 725 cm^{-1} is attributed to δ(NH) wagging vibration mode. It has been very well established that hydrazides show characteristic bands at 3320-3180, 1700-1640, 1633-1652, 1542-1502, 1150-1050 cm^{-1}, whereas diacetylhydrazides show at 3380-3280, 1742-1700, 1707-1683 cm^{-1}.[16] These vibration bands coincided with the present spectra quite well.

The ^{1}H NMR spectra of the both polymers are essentially the same except that **PHZ1** shows very broad absorption at 4.0-2.6 ppm due to the presence of water in the structure as HOD (Figure 4). The spectrum of **PHZ2** is very well resolved as being trimer (see below), but the spectrum of **PHZ1** is not so clear as being bimodal because of a mixture of polymers with different chain lengths.

The ^{1}H NMR spectrum of **PHZ2** is shown in Figure 5.

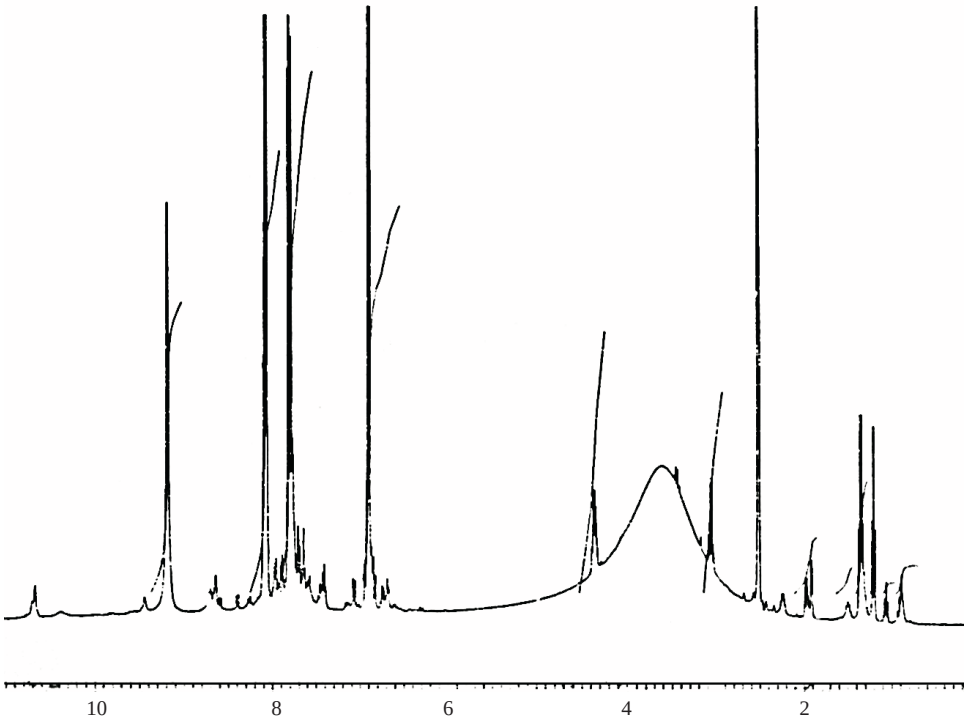


Figure 4. ^{1}H NMR spectrum of **PHZ1.**

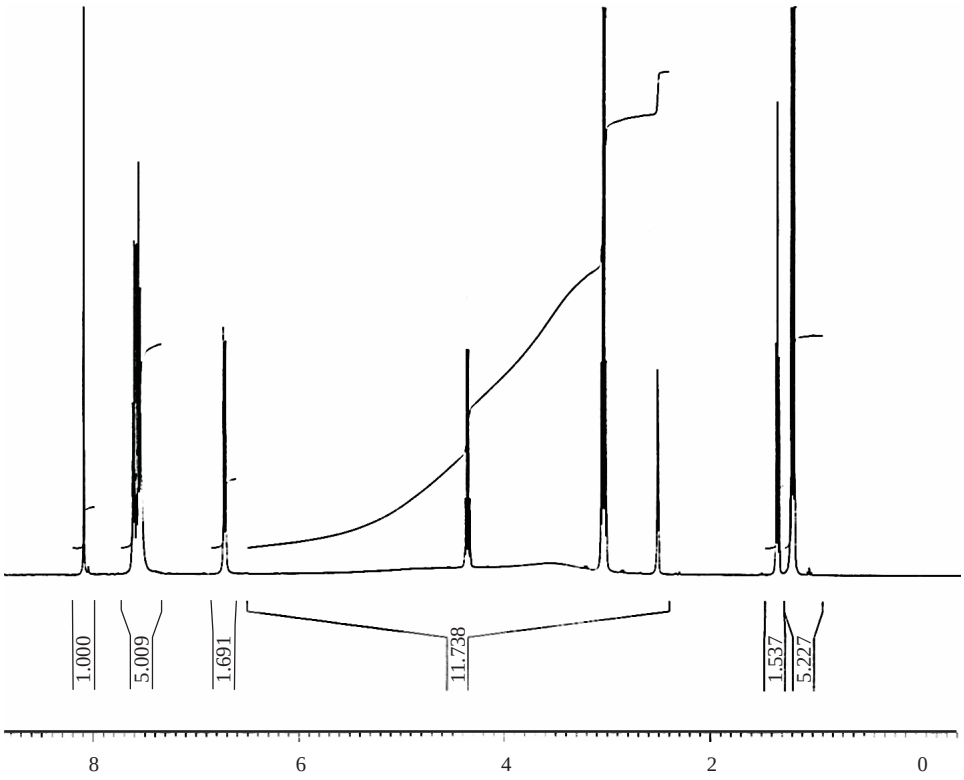


Figure 5. ^{1}H NMR spectrum of **PHZ2.**

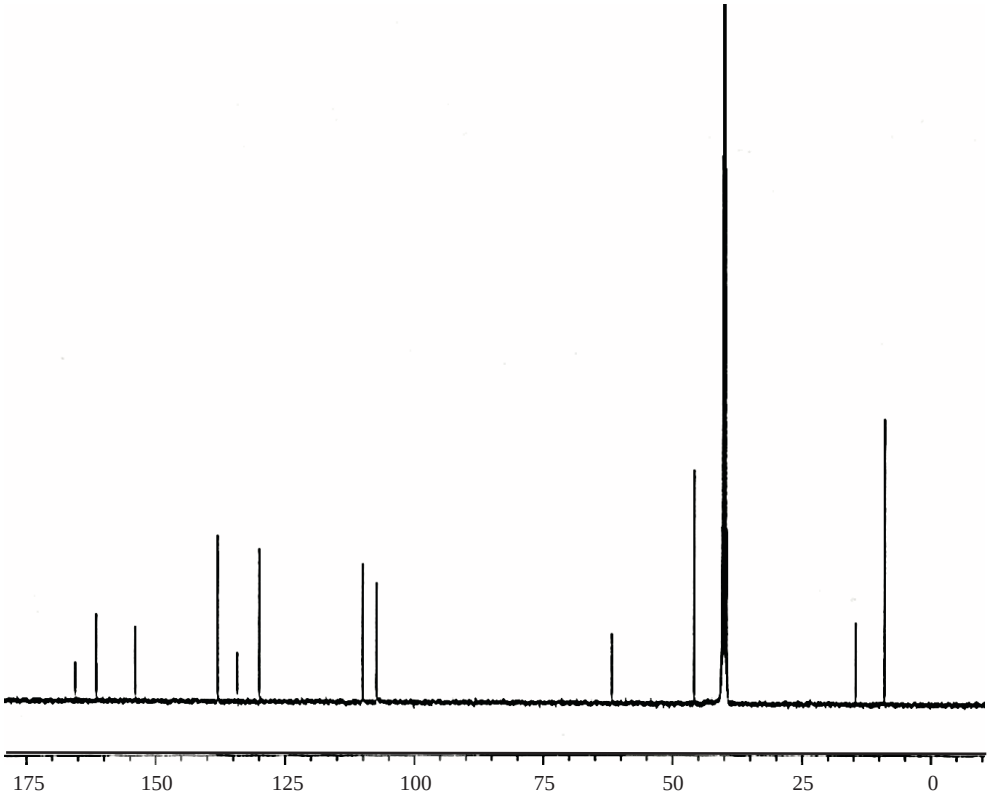


Figure 6. ^{13}C NMR spectrum of **PHZ2.**

The polymers were built up by symmetrical monomers which show C_2-symmetry revealed by both spectra. The aromatic ring is appeared as a singlet in the aromatic region at 8.1 ppm. The protons belonging to the bipyridine unit are observed in the expected range. The signal of NH proton is appeared at 10.7 ppm which is very characteristic for this type of amide protons. The end NH_2 signal is a broad singlet at 3.5 ppm in **PHZ1**. In the spectrum of **PHZ2**, there are 2 sets of peaks which can be attributable to ethanol at 4.4 and 1.3 ppm, and Et_3N peaks at 3.1 and 1.2 ppm. The structure was further characterized by ^{13}C NMR (Figure 6). The structure was confirmed by the presence of 12 peaks as expected. The carbon atoms of the pyridine rings at the end and in the chain should be different; otherwise, the spectrum should present only 7 signals due to symmetry.

The molecular weights of **PHZ1** and **PHZ2** were also determined by GPC analysis. The GPC chromatogram of **PHZ1** was also bimodal because of mixtures of polymers with different degree of polymerizations (Table 2). The GPC chromatogram of **PHZ2** was unimodal and indicated that product should form a trimer as **2-TPCl-2** with the calculated molecular weight of 562 in which the molecular weight of **2** is 216 g/mol and the molecular weight of **TPCl** is 203 g/mol. This value is in good agreement with the M_n value determined by GPC analysis.

Conclusion

Previously, a series of polyamides and polyesters based on 2,2′-bipyrdine-5,5′-dicarboxylic acid have been prepared using various polymerization methods and their metal complexes and photopyhsical properties were investigated. Here we successfully prepared novel polyamide and polyhydrazides based on 2,2′-bipyridine-

6,6′-dicarbonyl chloride and 2,2′-bipyridine-6,6′-dihydrazine, respectively. The structures of the polymers were confirmed by IR and NMR spectroscopies, and their molecular weights were determined by GPC. Usually high molecular mass polymers were obtained with low PD values showing the purity of the obtained polymers. The 6,6′-disubstituted bipyridine ligands show twisting around the central single bond due to steric hindrance so that metallo-supramolecular helices can be obtained by coordination of metal ions, since the polymers act as poly(bidentate) ligand. The coordination chemistry of the reported polymers and self-assembly properties of the copolymeric metal complex products may serve as subjects of future reports.

It is noteworthy that in the processes polymerization of **2** with **TPCl,** the increase in the monomer concentrations while keeping the mole ratio constant and the increase in temperature resulted in the formation of trimer as **PHZ2** as shown in Table 2. As a result, the degree of polymerization preferentially increases in a more diluted system at a lower temperature for the bipyridinyl monomers are associated with the solubility of the product.

Acknowledgments

This work was supported by the Turkish Scientific and Technical Research Council [TBAG-2450(104T060)].

References

1. S. C. Yu, S. Hou, and W. K. Chan, **Macromolecules 33,** 3259-3273 (2000)
2. W. W. Adams, R. K. Edy, D. E. McLemore, "**The Materials Science and Engineering of Rigid-Rod Polymers**" eds. Symposium Proceeding Vol. 34, Materials Research Society, Pittsburg, PA, 1989.
3. Z.-Q. Hu, H.-Y. Hu, C.-F. Chen, **J.Org.Chem. 71**, 1131-1138 (2006).
4. A. Abdolmaleki, **Polym. Degrad. Stab. 92**, 292-298 (2007).
5. P. G. Gervasi, S. D. Petris, D. Lupinacci, **Eur. Polym. J. 11,** 233-239 (1975).
6. N. A. Mohamed, A. O. Hamad Al-Dossary, **Polym. Degrad. Stab. 79**, 61-75 (2003).
7. A. H. Frazer, W. Sweeny, F. T. Wallenberger, **J. Polym. Sci. A2,** 1157-1169 (1964).
8. F. Higashi, S. C. Cho, H. Kakinoki, O. Sumita, **J. Polym. Sci, Polym. Chem. Ed. 15,** 2303-2309 (1975).
9. F. Frazer, F. T. Wallenberger, **J. Polym. Sci, Part A, 2,** 1825-1832 (1964).
10. B. Wang, M. R. Wasielewski, **J. Am. Chem. Soc. 119,** 12-21 (1997).
11. C.-A. Fustin, P. Guillet, U. S. Schubert, J.-F. Gohy, **Adv. Mater. 19,** 1665-1673 (2007).
12. Y. P. Wang, D. C. Neckers, **React. Polym., Ion Exch., Sorbents, 3,** 191-195 (1985).
13. Z. M. Michalska, B. Ostaszewski, K. Strzelec, **J. Organomet. Chem, 496,** 19-23 (1995).
14. T. Ogoshi, H. Itoh, K.-M. Kim, Y. Chujo, **Macromolecules 35,** 334-338 (2002).
15. S. Ogawa and S. Shiraishi, **J. Chem. Soc., Perkin Trans I** 2527-2529 (1980).
16. H. Günzler, H.-U. Gremlich, "**IR Spectroscopy**" Wiley-VCH, 2002.
17. W. B. Euler, **Polyhedron 10(8)**, 859-865 (1991).
18. S. C. Rasmussen, D. W. Thompson, V. Singh, J. D. Petersen, **Inorg. Chem. 35**, 3449-3450 (1996).
19. Z.-Q. Hu, H.-Y. Hu, C.-F. Chen, **J. Org. Chem. 71**, 1131-1138 (2006).
20. H. Jiang, V. Maurizot, I. Huc, **Tetrahedron 60**, 10029-10038 (2004).