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Synthesis and characterization of new polyamides bearing α,α′-xylyldithiophenoxide units in the main chain: Microwave irradiation, nanostructures

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ABSTRACT

New polyamides containing α,α′-Xylyldithiophenoxide Units were prepared under microwave irradiation and their solubility, thermal behavior, viscosities and nanostructures were evaluated. These polyamides showed good solubility in a series of organic solvents. The viscosities of these polyamides are in the range of 0.41-0.54 dl/g. Glass transition temperatures are in the range of 214-251°C. Temperatures for 10% weight loss (T10) are in the range of 286-323°C, temperatures for 50% weight loss (T50) are in the range of 463-535°C and char yields are in the range of 21-41%; and these results shows the thermal stabilities of the prepared polyamides. Supramolecular assemblies showed nanostructures.

KEYWORDS

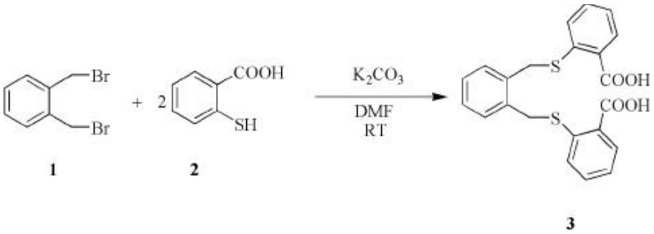
Polyamide;
Synthesis;
α,α′-Xylyne;
Thiosalysilic acid;
Thioether;
Nanostructure;
Nanoparticle.

INTRODUCTION

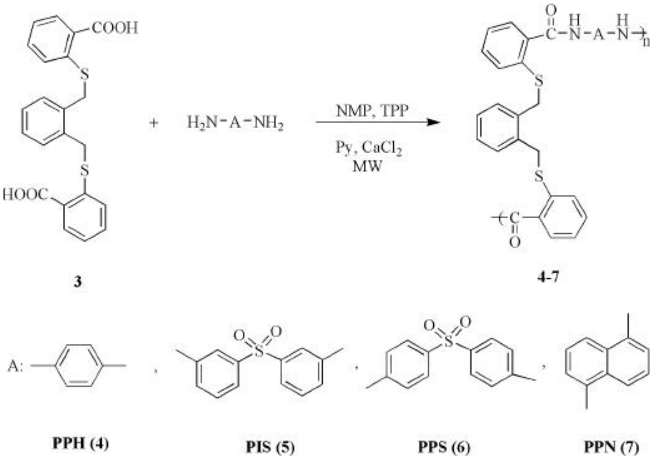
Polyamides are high performance polymers bearing the amide linkages in the polymer backbone. Aromatic polyamides are a class of high temperature resistance polymers with good chemical resistance, thermally stable, tough, translucent, semi-crystalline, low flammable, very good mechanical properties and moderately low cost[1-4]. However, because of their limited solubility in a series of organic solvents, high melting and glass transition temperatures, because of crystalline and close packing structures, they have difficulties in fabrication and processing. The introduction of flexible bonds into the rigid polymer backbone improves the solubility and melting behaviors[5-7]. However, some efforts in using monomers with bulky flexible side groups have been led to polymers with poor solubility in organic solvents[8]. Practically, introduction of a flexible bond into the polymer backbone is known to be effective in improving solubility and processability while maintaining the high thermal stability of the polymer[8].

The application of microwave irradiation in organic synthesis and material sciences has become increasingly popular, because it is an enabling technology for a large number of research areas such as general organic synthesis, drug discovery, polymer chemistry and nanotechnology[9]. By taking advantage of this efficient source of energy, compound libraries for lead generation and optimization can be assembled in a fraction of the time required by conventional thermal methods. Recently, thermally driven organic transformations take place by either of two ways: conventional heating or microwave accelerated heating. In the first way, the reaction mixture is slowly activated by a conventional external heat source. Heat is driven into the substance, passing first through the walls of the reaction vessel in order to reach the solvent and reactants. This is a slow and inefficient method for transferring energy into the reacting mixture. In the second way, microwaves couple directly with the microwave absorbing molecules of the entire reaction mixture, leading to a rapid rise in temperature of that molecules and as a result the matrix of reaction. The process is not limited by the thermal conductivity of the vessel, the result is an instantaneous localized superheating of any substance that will respond to either dipole rotation or ionic conduction and thus absorbs the microwave irradiation[9a].

In this research work new polyamides containing pyridine thioether units in the main chain were synthesized under microwave irradiation and characterized. They are soluble in a series of organic solvents and showed thermal resistance. SEM images of these polymers showed nanoparticle structures.



Scheme 1 : Synthesis of diacid (3).



Scheme 2 : Synthesis of polyamides (4-7).

RESULTS AND DISCUSSION

The diacid monomer was synthesized by a one-step route, as shown in Scheme 1. In this route nucleophilic reaction of thiosalicylic acid (2) with dibromide (1) in DMF afforded diacid monomer (3). The structure of diacid was confirmed by IR, ^{1}H NMR and mass spectroscopy and elemental analysis. The FTIR spectrum of diacid (3) is appeared in Figure 1.

Among various methods for polyamidation reaction, direct polycondensation methods have been developed by several investigators and especially by Yamazaki and Higashi[10-13]. Direct polycondensation of dicarboxylic acid (3) with diamine using TPP and pyridine as condensing agent under microwave irradiation (MW) to form amide bonds is an efficient route to offord polyamides of moderate to high degree of polymerization on a laboratory scale. All of the polymerization reactions were carried out in NMP in the presence of $CaCl_2$ and preceded homogeneously. The synthetic route and designation of polyamides are shown in Scheme 2. The polyamides were obtained in good yields (TABLE 1, 94-98%) and had inherent viscosities ranging between 0.41 and 0.54 dL/g. The structures of polyamides were confirmed by elemental analysis (TABLE 2), FTIR and ^{1}H-NMR spectroscopy (TABLE 3). The FTIR spectra of the polyamides exhibited the characteristic absorption bands (TABLE 3). The FTIR spectrum of polyamide (4, PPH) is appeared if Figure 2. The total protons in the ^{1}H NMR spectra are consistent with the proposed chemical structures of the polymers (TABLE 3).

The solubility behavior of the new polyamides was determined for the powder samples in excess solvents. All the polyamides exhibited excellent solubility in the polar aprotic solvents such as NMP, DMAc, N, N-dimethylformamide, dimethyl sulfoxide (DMSO) at room temperature, and were soluble in THF under heating conditions (TABLE 5). The solubility of an aromatic polyamide with an all-meta aromatic ring substitution in the diamine residue can be different from an aromatic polyamide with an all para aromatic ring substitution. However, the solubility of the synthesized polyamides was identical due to the presence of rigid diamine residue. This could be because of the diamine residue is sufficient smooth structure to improve the interchain interactions in the backbone. the presence of flexible CH_2 groups in the polymer backbone have opposite effect in comparison with symmetric and smooth diamines and then the interchain interactions reduce and as a result solubility improves. Polar amide groups in the polymer chain can also form the intramolecular hydrogen bondings, because of ortho substitution of diacid (3) and this phenomenon lowers the interchain interactions and thus crystallinity and as a result improves the solubility. A dense chain packing of the polymer chains was probably disturbed by the flexible groups; consequently, the solvent molecules were able to penetrate easily to soluble the polymer chains.

The thermal behavior of the polyamides was evaluated by DSC and TGA. The glass transition temperatures (T_g) of the polyamides, as determined by DSC, are between 214 and 251°C as shown in TABLE 4. Among all the synthesized polyamides, (PPS,6) based on 4,4'-diaminodiphenyl sulfone content in the main structural unit showed the highest Tg value because of the highest rigidity, which inhibited the molecular motion. In general, polymers with more flexible groups in the main chain leads to lower Tg's than polymers without these groups due to the greater interchain distance and interactions, which lowers the strength of the amide–amide hydrogen bonds that are partly responsible for the generally high Tg's of these aromatic polyamides. The high Tg of the polyamides can be due to the high barrier for segmental mobility as a result of strong main chain-main chain interaction through H-bonding. As we expected, Tg of the polyamides showed dependence on the structure of the diamine component, and decreased with increasing flexibility of the polyamides main chain.

The thermal stability of polyamides was investigated by TGA in a heating program under Ar to elucidate how the chemical structure influenced the value of the decomposition temperatures. TGA data are listed in TABLE 4. The temperatures of 10% weight loss (T10) are in the range of 286 and 323°C. The breaking of a bond in the main chain structure gives rise to the thermal degradation of the aromatic polyamides. The temperatures of 50% weight loss (T50) are in the range of 463 and 535°C. To compare thermal behavior, the breaking of a bond probably in the main chain of these polyamides, because of flexible bonds, caused these polymers to have lower thermal stability than the all aromatic polyamides (aramids). In addition, the residual weight retentions for the resulting polyamides were in the range of 21–41 % at 550 °C, implying that these polyamides possess reasonable thermal stability.

The surface morphology of polyamides was investigated using scanning electron microscopy and their SEM images show the nanostructures (Figures 4, 5, 6 and 7).

EXPERIMENTAL

The reactions for the synthesis of monomer were carried out in an efficient hood cupboard. All the materials were purchased from Merck, Fluka, Across Organics and Aldrich chemical companies. N-Methyl-2-pyrrolidinone (NMP, Merck) and pyridine (Py, Merck) were purified by distillation under reduced pressure over calcium hydride and stored over 4A ° molecular sieves. Triphenyl phosphite (TPP, Merck) was purified by fractional distillation under vacuum. Reagent grade aromatic diamines (Aldrich) including 1,5-diaminonaphthalene (DAN), 3,3'-diaminodiphenyl sulfone (MDAS) and 4,4'-diaminodiphenyl sulfone (PDAS) were recrystallized from ethanol. p-Phenylene diamine (PPD) was purified by sublimation. The melting points (uncorrected) were measured with a Barnstead Electrothermal engineering LTD 9100 apparatus. Elemental analysis was performed by a CHN-O- Rapid Heraeus elemental analyzer. FT-IR spectra were recorded in potassium bromide pellets on a Bruker apparatus. The ^1H NMR spectra were obtained using BRUKER AVANCE DPX 300 MHz and BRUKER AVANCE DrX 500 MHz apparatus. Mass spectra were obtained with Shimadzu GC-MS-QP 1100 EX model. Scanning electron micrograph (SEM) images were obtained using a XL30 (Philips) apparatus. The MicroSYNTH system of Milestone which is a multi-mode platform and equipped with a magnetic stirring plate was used for the synthesis. We used the high-pressure vessel (teflon (TFM) inserts) (vessel volume 100 mL, max pressure 1450 psi, max temperature 300 ºC). Temperature is controlled internally by fiber optic probe in one control reference vessel. Inherent viscosities ($\eta_{inh} = \ln \eta r/c$ at a concentration of 0.5 g dL^{-1}) were measured with an Ubbelohde suspended-level viscometer at 30 ºC using DMSO as solvent. Thermogravimetric analysis (TGA) was recorded on a V 5.1A DuPont 2000 system under argon atmosphere at a heating rate of 10 ºC Min.$^{-1}$. Differential scanning calorimetry (DSC) recorded on a V 4. OB DuPont 2000 system under argon atmosphere at a heating rate of 10 ºC Min.$^{-1}$.

Synthesis of benzodiacid (3, BDA)

To the mixture of 1 (*α,α′-Xylyldibromide*, 0.264 g, 1 mmol) and DMF (20 mL) was added thiosalysilic acid (0.308 g, 2mmol) and K_2CO_3 (0.56 g, 4mmol) at room temperature. The mixture was stirred at room temperature for 24h. After completion of the reaction (monitored by TLC), water was added and the mixture was nutralized using HCl solution. The resulting precipitate left for 12h and then filtered. Crystallization in ethanol afforded diacid as a white powder in 97% yield and melting point of 204-205ºC (uncorrected); IR (KBr): 2964, 2639, 1678, 1253, 1052, 740 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 4.32 (s, 4H), 7.21 (t, 2H, J=6 Hz), 7.28 (t, 2H, J=3 Hz), 7.47 (s, 6H), 7.89 (d, 2H, J=6 Hz), 12.36 (s, 2H) ppm; MS (EI) m/z (relative intensity %): 395 [M-15]$^+$ (6%), 362 (2%), 339 (3%), 317 (8%), 257 (42%), 228 (48%), 179 (27%), 151 (26%), 121 (100%), 105 (29%), 91 (49%), 72 (56%), 28 (42%); Analytical calculated for $C_{22}H_{18}O_4S_2$ (410.51): C, 64.37; H, 4.42; Found, C, 64.39; H, 4.41.

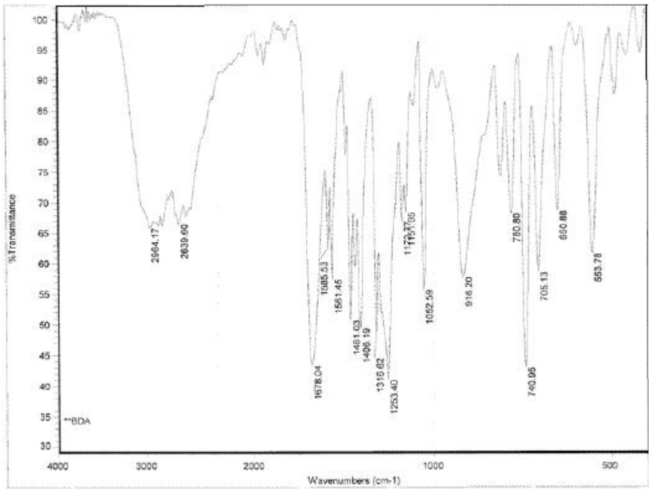


Figure 1 : FT-IR spectrum of benzodiacid (3, BDA).

Synthesis of polyamides

Polyamides were synthesized by the phosphorylation reaction of diacid (3, BDA) with various diamines as shown in Scheme 2. A typical example for the preparation of polyamides is given. A mixture of 3 (1 mmol, 0.42 g), p-phenylenediamine (1 mmol, 0.11 g), 0.3 g of $CaCl_2$, 0.6 mL of TPP, 0.5 mL of pyridine, and 4 mL of NMP were added to the quartz tube and irradiated under microwave in 600W for 9 Min. (3×3 Min.) and the rest time of 5 Min. After cooling at room temperature, the resulting viscose reaction mixture was poured into 300 mL of boiling methanol. The resulting crude product was precipitated and then filtered. The resulting polymer was washed with hot methanol (50 mL), hot water (twice, 50 mL) and then hot methanol (50 mL), respectively; and dried under vacuum at 100 ºC overnight. The yields were almost quantitative. Thermal properties, viscosity and solubility of these polyamides were reported in the following TABLES and Figures.

TABLE 1 : Inherent viscosity and the yields of polyamides.

Polymer	Yield (%)	η_{Inh}(g/dL)^a
PPH (4)	94	0.51
PIS (5)	96	0.58
PPS (6)	98	0.64
PPN (7)	97	0.57

[a] Measured at a polymer concentration of 0.5 g/dL in DMSO solvent at 30 ºC.

TABLE 2 : Elemental analyses of polymers.

Polymer	Formula	Elemental Analysis					
		Calculated (%)			Found (%)		
		C	H	N	C	H	N
PPH (4)	$C_{28}H_{22}N_2O_2S_2$	69.68	4.59	5.80	69.73	4.67	5.91
PIS (5)	$C_{34}H_{26}N_2O_4S_3$	65.57	4.21	4.50	65.58	4.26	4.55
PPS (6)	$C_{34}H_{26}N_2O_4S_3$	65.57	4.21	4.50	65.60	4.24	4.53
PPN (7)	$C_{32}H_{24}N_2O_2S_2$	72.15	4.54	5.26	72.23	4.59	5.34

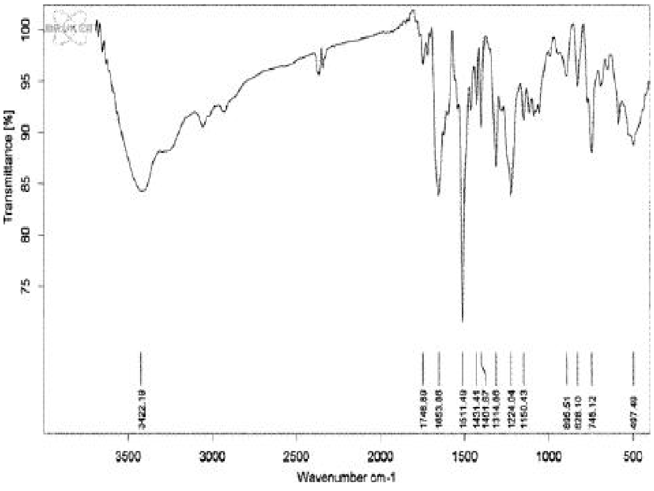


Figure 2 : FT-IR spectrum of polyamide (4, PPH).

TABLE 3 : Spectral data of polymers.

Polymer	IR (cm^{-1})	^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm)
PPH (4)	3422, 2460, 1653, 1511, 1401, 1314, 1224, 745.	4.34 (s, 4H), 7.16-7.38 (m, 10H), 7.49 (s, 3H), 7.65 (s, 3H), 10.33 (s, 2H).
PIS (5)	3311, 3258, 2458, 1674, 1576, 1523, 1341, 1314, 1155, 1103, 742.	4.34 (s, 4H), 7.21 (t, 2H, J=6Hz), 7.28 (t, 2H, J=3Hz), 7.46-7.49 (m, 8H), 7.75 (m, 4H), 7.91 (d, 2H, J=6Hz), 8.26 (s, 2H), 10.82 (s, 2H).
PPS (6)	3305, 2471, 1665, 1588, 1521, 1398, 1319, 1148, 835, 739.	4.29 (s, 4H), 7.10 (b, 3H), 7.20-7.25 (m, 4H), 7.31-7.33 (m, 2H), 7.44 (d, 2H, J=5Hz), 7.51 (dd, 3H, J= 5,10Hz), 7.88-7.94 (m, 6H), 10.83 (s, 2H).
PPN (7)	3458, 3367, 2421, 1679, 1612, 1073, 1021, 758.	4.35 (s, 4H), 7.24 (dd, 2H, J=4,10Hz), 7.34 (dd, 2H, J=4, 7Hz), 7.42-7.46 (m, 2H), 7.54 (s, 6H), 7.91 (d, 2H, J= 7Hz), 7.95-7.98 (m, 4H), 10.35 (s, 2H).

TABLE 4 : Thermal properties of polyamides.

Polymer	T_g (°C)	T_{10}^{a} (°C)	T_{50}^{b} (°C)	Char yields^c (%) 550 °C
PPH (4)	230	296	472	23
PIS (5)	245	314	512	37
PPS (6)	251	323	535	41
PPN (7)	214	286	463	21

TABLE 5 : The solubility of polyamides (4-7).

Polymer^a	NMP	DMAc	DMF	DMSO	m-Cresol	THF
PPH (4)	++	++	++	++	±	+
PIS (5)	++	++	++	++	+	+
PPS (6)	++	++	++	++	±	+
PPN(7)	++	++	++	++	+	+

(++) Soluble at room temperature; (+) soluble upon heating; (±) partially soluble; ^{a}Solubility measured at a polymer concentration of 0.05 g/ml.

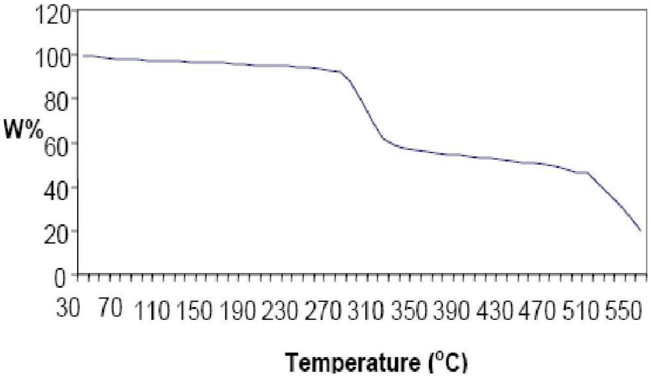


Figure 3 : TGA of polyamide (4, PPH).

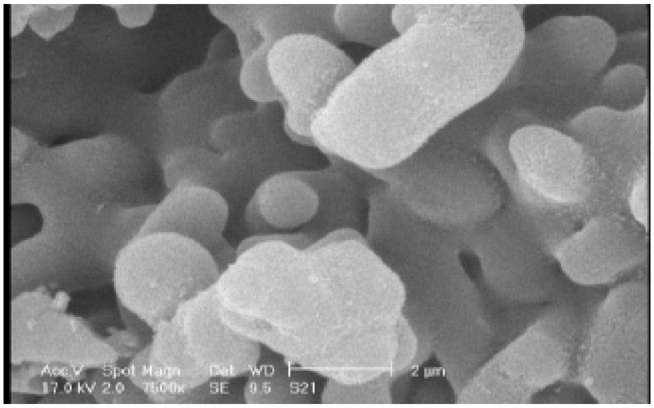


Figure 4 : SEM image of polyamide 4 (PPH).

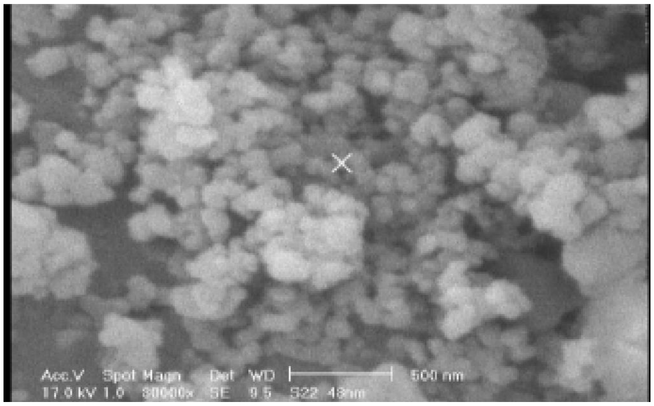


Figure 5 : SEM image of polyamide 5 (PIS).

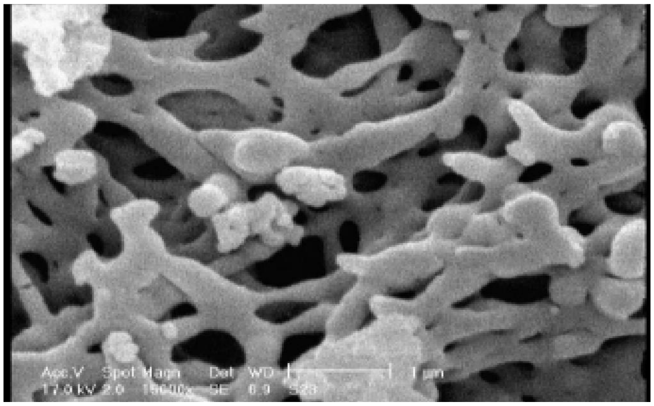


Figure 6 : SEM image of polyamide 6 (PPS).

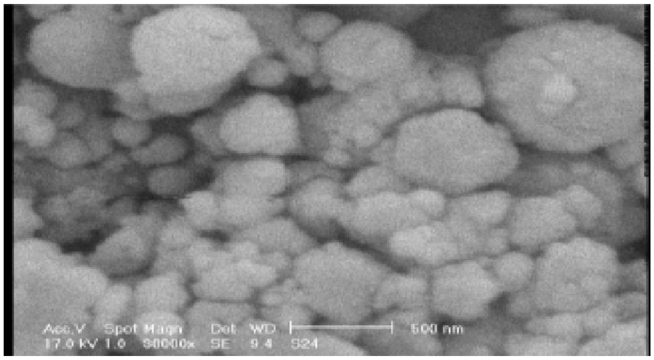


Figure 7 : SEM image of polyamide 7 (PPN).

CONCLUSION

A novel diacid containing flexible groups in the main chain has been synthesized in good yields and high purity from readily available reagents. A series of polyamides have been prepared from this diacid and various aromatic diamines via the direct phosphorylation polycondensation. The introduction of unsymmetric bonds into the polymer backbone led to improvement in solubility of the polymer, because of decrease in the ability for polymer chains to pack and reduction of interchain interactions, and this also increased Tg of the polymer as a result of decrease in the segmental mobility due to flexible groups and less main chain-main chain interaction through H-bonding. Most of these polymers exhibited a desired combination of properties requiring high-performance materials that include high thermal stability, and excellent solubility in organic solvents for fabrication and applications. The nanostructure of these polymers shows the less interchain interactions and more solubility.

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