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Synthesis and Properties of Polyimides from 1,3-di(*p*-dimethylaminobenzyl)-imidazolidine-2-thion

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SUMMARY

A synthetic strategy is presented that allows the preparation of dimethylamino functionalized heterocyclic system 1,3-di (*p*-dimethylaminobenzyl)-imidazolidine-2-thion that was then used to prepare polyimides by the two-stage polycondensation method. The key to this success was the development of an efficient procedure leading highly pure dimethylamino monomer. Polyimides derived from 1,3-di(*p*-dimethylaminobenzyl)-imidazolidine-2-thion and commercial dianhydrides exhibited excellent solubility in various polar solvents. These polymers showed glass transition temperatures between 290-360°C, and initial decomposition temperature 490-485 °C and 10% mass loss ranging from 505-575°C in air.

INTRODUCTION

Polyimides are one of the most useful engineering plastics because of their superior thermal stability, inherent fire and good chemical resistance [1-5]. Most of these polyimides are prepared by two-stage condensation process in which a poly(amic-acid), formed from aromatic diamines and aromatic dianhyrides, is converted to the polyimide by dehydration.

However, their poor solubilities in common organic solvents and their infusibilities tend to limit their application in many fields. Improved solubility can be achieved by the incorporation of flexible groups into the polymer backbone to either reduce stiffness or lower the interchain interactions [6-12]. The range of topics covered and exploited by researchers [13-15] demonstrates the continued interest in polyimides. The ordering and varying of backbone functions have a profound effect on the final properties of the polymer. Hexafluoroisopropylidene [16] functions have been incorporated into polyimides to seek improved solubility and unique charge-storage properties, the charge retention in thin polymer films have been extensively studied. Incorporation of flexible segments, such as –O-, $-SO_2-$, CH_2-, $-C(CF_3)_2-$ and bulky pendant groups have been successful to increase solubility however accompanied by a generally decrease in thermal properties. 1,1-bis(4-aminophenyl) cyclohexene, 4,4'-bis(p-aminophenoxy methyl)-1-cyclohexene [17] and various methyl substituted cyclohexene derivatives have also been reported to form soluble polyimides with acceptable Tg's and oxidative stability. Here, we describe the preparation of 1,3-di(*p*-dimethylaminobenzyl)-imidazolidine-2-thion and its polyimides with commercial dianhydrides. The synthetic approach here described offers a twofold advantage over conventional polyimides. First, tractable polymers can be synthesized without lowering thermal and heat stability, and secondly, because of the bulky heterocyclic group the stiffness has been lowered, the inter- and intrachain interactions reduced which have been resulted in an increase in solubility in dipolar aprotic media.

EXPERIMENTAL

Materials

All chemicals were purchased form Aldrich and used after purification. NMP was distilled over CaH_2 under reduced pressure and stored over 4Å molecular sieves. Reagent grade aromatic dianhydrides such as pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyl tetra carboxylic dianhyride (BTDA), 4,4'-oxydiphthalic anhydride (ODPA) were sublimed at 250°C under reduced pressure, 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BPDA) was used after crystallization in acetic anhyride. All dianhydrides were dried under vacuum at 120°C prior to use.

Characterization and synthesis

Infrared spectra were recorded on ATI UNICAM systems 2000 Fourier transform spectrophotometer (FT-IR). Spectra of the solids were carried out with KBr pellets. ^1H NMR (300.133 MHz) and ^{13}C NMR spectra (75.47 MHz) were recorded on a Bruker AM 300 WB FT spectrometer with δ referenced to $CDCl_3$ for monomers and DMSO-d^6 for polymers. Elemental analysis were performed by the TÜBİTAK (Ankara). Differential scanning calorimeter (DSC), differential thermal analysis (DTA) and thermogravimetry (TG) were performed with Shimadzu DSC-60, DTA-50 and TGA-50 thermal analyzers, respectively.

Inherent viscosities were measured at a concentration of 0.5 g/dL in NMP at 30°C using an Ubbelohde viscometer.

1,2-Bis(p-dimethylaminobenzylideneamino)ethane, (1a)

p-Dimethylaminobenzaldehyde (20g, 134 mmol) in ethyl alcohol, ethylenediamine (4.5g, 75 mmol) was added to this solution in portion. Stirred under nitrogen atmosphere with reflux for an hour and the yellow precipitate formed was collected by filtration and washed with ethyl alcohol and dried in air.

The yield was 21.1g (97%). m.p. 179-180°C. ^1H NMR: 6.64 (d, *J*8. 8),7.56 (d, *J*8. 8); 2.95(s) (-N $(CH_3)_2$), 3.86(s) (-NCH_2CH_2N-); 8.15 (s) (-CH=N-).

Elemental Analysis for $C_{20}H_{26}N_4$ (322.45) : C, 73.97 (74.50); H, 7.25 (8.12); N, 16.95 (17.37).

1,2-Bis(p-dimethylaminobenzylamino) ethane, (2a)

1a (4.8g, 14.8 mmol), Pd/C (0.5g) and toluene (100 ml) were placed in a Parr reactor, the pressure was set to 300 psi under H_2 gas, heated to room temperature. When the pressure was constant, the reactor was opened the Pd/C filtrated, excess toluene removed by distillation. Hexane was added to this mixture and formed crystals were collected by filtration, and finally dried in vacuum.

The yield was 4.1g (85%); m.p. 72-73°C.
^{1}HNMR: 6.64 (d, *J*8, 7)-7.14 (d, *J*8.7); 2.89(s) (-N (CH_3)$_2$), 2.70(s) (-NCH_2CH_2N-); 3.60(s) (-CH_2 (C_6H_4)-; 1.41 (s) (-N*H*CH_2).
Elemental Analysis for $C_{20}H_{30}N_4$(326.47): C, 73.73 (73.58); H, 8.38 (9.26); N, 16.27 (17.16).

1,1',3,3'-Tetra(p-dimethylaminobenzyl)-[2,2']biimidazolydene, (3a)

2a (3.1g, 9.5 mmol) was dissolved in dry toluene (15mL) and 20% excess of *N,N*-dimethylformamide dimethyl acetal (1.37 g, 11.5 mmol) was added. The solution was heated to 80°C in a water bath for 3h, then, within 2.5h, $HNMe_2$ and MeOH were distilled as by products. The temperature was raised to 110°C for 1.5h. Toluene was removed by distillation and hexane added to the mixture. Precipitated crystals were collected by filtration, and dried in vacuum.
The yield was 2.76g 85%, m.p. 144-145°C.
^{1}HNMR: 2.99(s) (-NCH_2CH_2N-); 4.61 (s) (C6H4CH2); 2.51(s) (-N (CH_3)$_2$); 6.61(d, *J*8.5), 7.28 (d, *J*8.4).
^{13}C NMR: 150.2 C_2; 49.3 (-NCH_2CH_2N-); 56.1 (C6H4CH2); 40.6 (-N (CH_3)$_2$); 113.3; 128.9; 129.8; 130.4.

1,3-Di(p-dimethylaminobenzyl)-imidazolidine-2-thion, (4a)

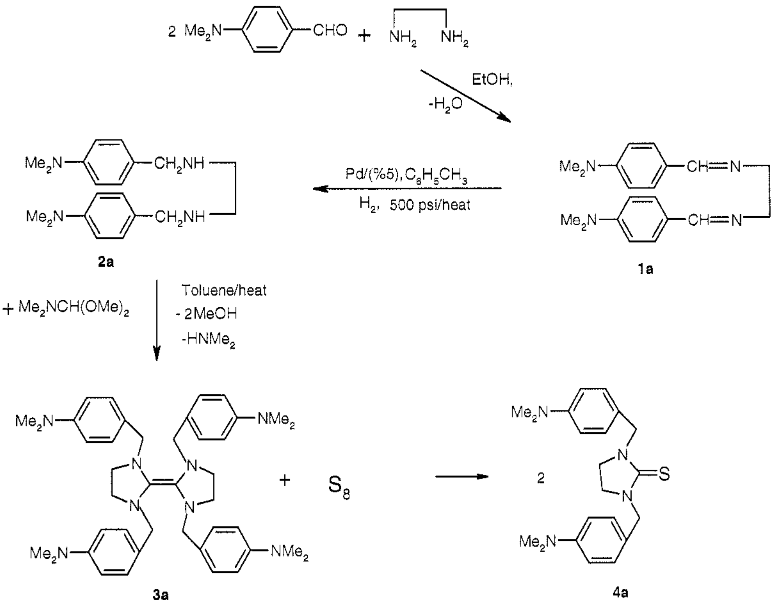
3a (0.69g, 0.103 mmol) was dissolved in dry toluene (10 ml) and to this solution sublimed sulfur (0.066g, 2.06 mmol) was added. The red solution was heated 1.5h in a water bath at 80°C. The mixture was cooled to room temperature, 10 mL hexane was added and the crude product was obtained by cooling at -20°C. The creamy product was washed several times with toluene and crystallized from hexane.
The yield was 0. 63g (83%), m.p. 151-152°C.
^{1}HNMR: 3.29(s) (-NCH_2CH_2N-); 4.75(s) (C_6H_4CH_2); 2.90(s) (-N (CH_3)$_2$); 6.66 (d, *J* 8.7) -7.20 d, *J* 8.5).
^{13}C NMR: 182.5 (C_2); 45.6 (-NCH_2CH_2N-); 51.6 ($C_6H_4CH_2$); 41.1 (-N (CH_3)$_2$; 113.0-124.6-129.9-150.6 (aromatic carbons).
Elemental Analysis for $C_{42}H_{56}N_8$ (672.94): C, 68.57(68.44); H, 6.52(7.54); N, 15.40(15.21).

Synthesis of polyimides

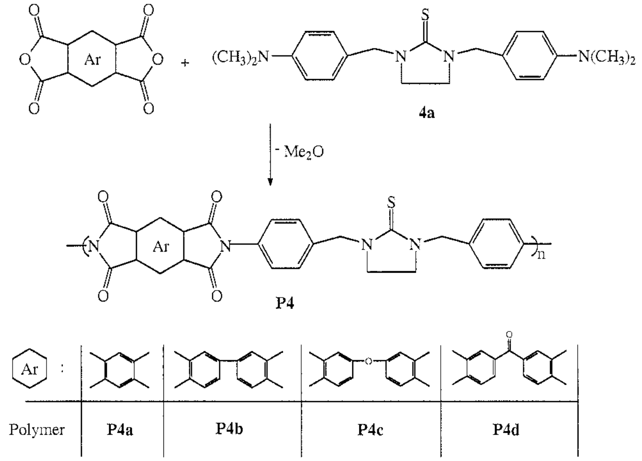
A typical polyimide (**P4a**) synthesis was performed as follows: monomer **4a** (1.41g, 4.15mmol) was dissolved in 15mL NMP in a 100 mL schlenck tube equipped with an argon line, overhead stirrer, a xylene filled Dean-Stark trap, and a condenser. PMDA (0.9g, 4.15 mmol) was added to the amine solution that was stirred overnight to give a viscous solution. The mixture was heated to 70°C, 5mL xylene was added, and the temperature was raised to reflux for 3h. Following the removal of xylene by distillation, the reaction mixture was cooled at room temperature and precipitated into large excess of methanol. The yellow product was isolated and dried at 100°C under vacuum and then 200-250°C under nitrogen for 2h. The yield was 88.7%.
^{1}HNMR for **P4a** in DMSO-d^6: 3,26(s) (-NCH_2CH_2N-); 4,72(s) (C_6H_4CH_2); 6,70 (d, *J* 8,6) -7,60 (d, *J* 8,6) (C_6H_4); 9.58 (s) (C_6H_2 in pyrromellitic group).

RESULTS AND DISCUSSION

1,3-Di-*p*-dimethylaminobenzylimidazolidine-2-thion, **4a,** has been synthesized as shown in Scheme 1. The dimethylamino groups were conveniently converted to the polyimides in a pure form and a high yield via one pot procedure



Scheme 1. Synthetic route for the preparation of the monomers



Scheme 2. Synthetic route for the preparation of polyimides

Synthetic outline for he preparation of the polyimides were given in Scheme 2.

Polyimides **P4c** and **P4d** showed good solubility in THF, NMP, DMF, DMSO and

$CHCl_3$, while **P4a** and **P4b** had excellent solubility in polar aprotic solvents as given in Table 1.

The high solubility of the polyimides is attributed to the thion group that reduced the stiffness and inter- and intrachain interaction.

Table 1. Some physical properties of the synthesized polyimides

	Polymer	P4a	P4b	P4c	P4d
	Yield	88.7	82	83	79
	d (g/cm^3)[a]	1.22	1.31	1.41	1.27
	η (dL/g)[b]	1.81	1.92	2.02	1.84
	T (°C)[c]	575	543	512	505
	Char yield[d] (%)	32	27	29	25
Thermal Properties	Endset	383.55	312.11	-	302.12
	Onset	340.72	267.51	-	256.45
	Transition	-3.43	-1.60	-	-2.51
	Tg[e] (°C)	358.95	308.23	-	289.56
Solubility	NMP	+	+	+	+
	DMF	+	+	+	+
	DMAc	+	+	+	+
	Ether	-	-	-	-
	THF	-	±	-	-
	$CHCl_3$	-	-	+	+
	DMSO	+	+	+	+

[a] Determined by suspension method at 30°C. [b] Measured at a concentration of 0.5 g/dL in NMP at 30°C using an Ubbelohde viscometer. [c] Temperature of 10% weight loss was assessed by TGA at a heaing rate of 10 °C/min. in N_2 [d] Assessed by TGA at 800 °C in N_2 atmosphere. [e] Determined by DSC in N_2 atm.

The FT-IR spectra (Figure 1) showed that aliphatic C-H stretching frequencies were appeared between 2850-2890 cm^{-1}, 1720-1730 cm^{-1} sym. imide ν (C=O), 1725 cm^{-1} (s) asym imide ν (C=O) stretching 1790-1765 cm^{-1}, C-N imide ring stretching 1360 cm^{-1}, whereas imide ring deformation appeared near 1070 cm^{-1} and C-N bending at 730-760 cm^{-1} . Typical poly(amic acid) absorption bands at 3400-2900 cm^{-1} corresponding to amide (-NH-) and acid (-OH) stretching, 1720 cm^{-1} corresponding to C=O stretching of carboxylic acid, 1540 cm^{-1} corresponding to the C-N stretching of amide were not observed indicating that the polymerization mechanism with this type of monomers differ.

The polyimides synthesized via the one-pot synthetic method **P4a** , **P4b, P4c** and **P4d** are well dissolved in polar aprotic solvents at elevated temperatures and form flexible and tough films by casting. ^{1}H- NMR spectra of the polyimides showed no amid and acid protons, indicating full imidization. Also, TGA and DSC measurements that did not show any transition corresponding to the imidization imply that polyimides were fully imidized.

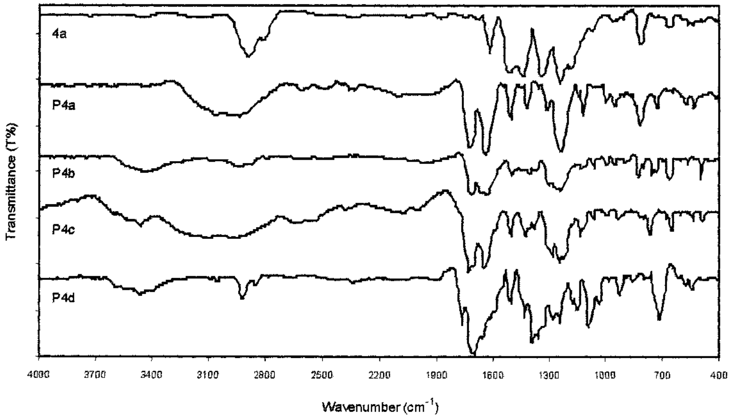


Figure 1. FT-IR spectra of the monomer and the polyimides P4a to P4d

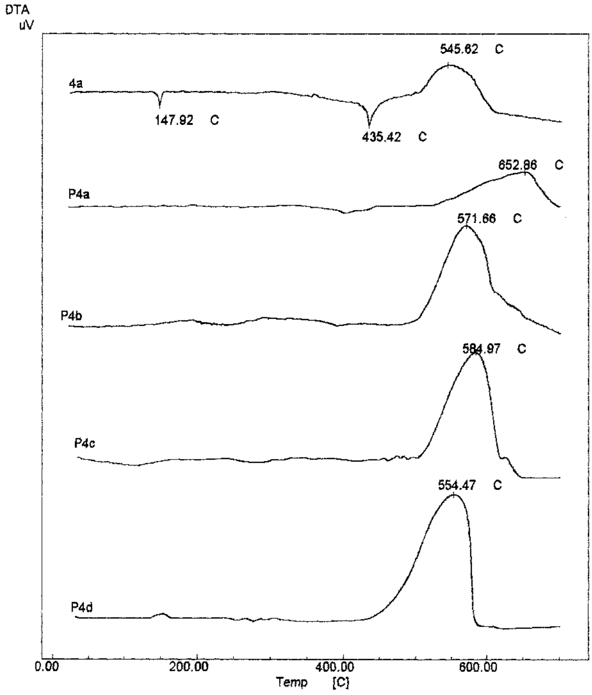


Figure 2. DTA pattern of the monomer 4a and the polyimides P4a to P4d at a heating rate of 10 °C/min in air

Interestingly, the solubility of the polyimides prepared by the one-step imidization method increased and became comparable to that of the polyimides prepared by the conventional monomers via poly(amic) acid step followed by thermal cyclization. One of the plausible explanations is that introducing the imidazoline segment may invoke a chain ordering of the polyimides that increases chain to chain interactions. As mentioned above, polyimide synthesized from 4c and 4d and ODPA and BPDA respectively has the best solubility enhancement effect of oxygen and carbonyl groups. Thermal properties of the polyimides (Figure 2 and 3) were evaluated by TGA, DSC and DTA. The thermal properties of the polyimides are summarized in Table 1. Glass transition temperatures (Tg's) of the polimides determined by DSC were found to be in the range of 289 to 358 °C. No melting endotherm peak was observed from the DSC curves. The DTA and DSC measurements also revealed the amorphous nature of the polyimides. The lowest Tg was observed for the most flexible dianhyride BPDA , structure. As could be expected PMDA , exhibited the highest Tg. The temperatures at 10%mass loss (Td's) examined by thermogravimetric TGA analysis, showed values ranging 505-575 °C in nitrogen atmosphere. The residual masses determined by means of TGA at 800°C were ranged from 25 to 32%.

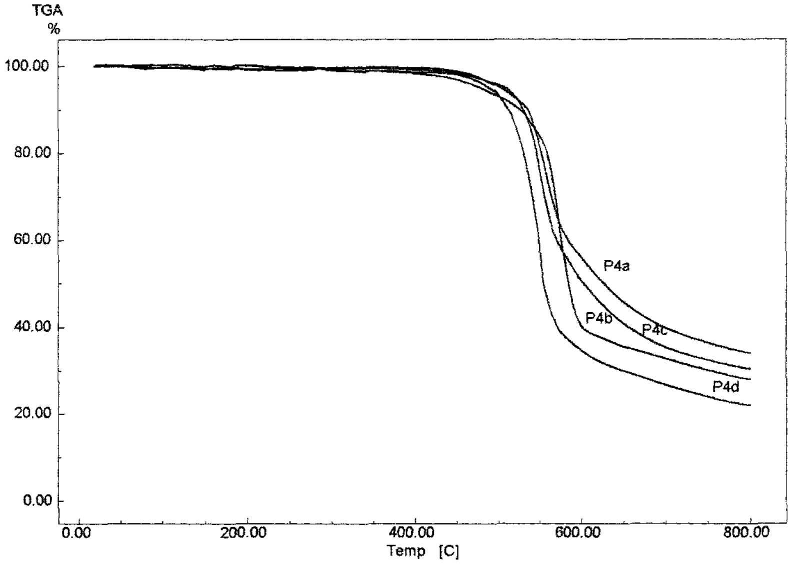


Figure 3. TGA pattern of the polyimides P4a to P4d at a heating rate of 10 °C/min in nitrogen

CONCLUSION

In summary, a new series of polyimides containing 1,3-di (*p*-dimethylaminobenzyl)-imidazolidine-2-thion, are prepared by using the one-pot procedure in polar protic solvents. The polyimides prepared were largely soluble in polar solvents at elevated temperatures. The polyimides have excellent thermal properties, and their thermal properties are comparable to those of polyimides prepared from diamine monomers. Further studies on the mechanism are in progress in our laboratory.

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References

1 Mittal Kl (ed) (1984) Polyimides: Synthesis, characterization and applications, 1 & 2. Plenum, NY;
2 Feger C, Khojasteh MM, Htoo MS (ed) (1993) Advances in polyimide Science and Technology, Technimin, Lancaster, PA
3 Hasegawa M, Horie K (2001) Prog. Polym. Science 26:259
4 Mallakpour SE, Hajipour AR, Fard RR (2001) Journal of Applied Polymer Science 79:1716
5 Chang J-H, Park KM, Lee IC (2000) Polymer Bulletin 44: 63
6 Kim YS, Jung JC (2000) Polymer Bulletin 45: 311
7 Tamai S, Kuroki T, Shibuya A, Yamaguchi A (2001) Polymer 42: 2373
8 Pyo SM, Kim SI, Shin TJ, Ree M, Park KH, Kang JS (1999) Polymer 40(1): 125
9 Chang J-H., Chen MJ, Farris RJ (1998) Polymer 39: 5649
10 Hou H (1999) European Polymer Journal 35:1993
11 Zheng HB, Wang ZY (2000) Macromolecules 33(12): 4310
12 Tamai S, Yamashita A, Yamaguchi A (1998) Journal of Polymer Science Part A: Polymer Chemistry 36: 1717
13 Vora RH, Goh SH, Chung T-S (2000) Polymer Engineering and Science 40(6): 1318
14 Ozdemir I, Cetinkaya B, Seckin T, Koytepe S (2002) J. of Molecular Catalysis A: Chemical 179: 263
15 Huang W, Yan D, Lu Q, Tao P (2002) Journal of Polymer Science Part A: Polymer Chemistry 40:229
16 Sekiguchi H (1998) Chemistry of Materials 10(3): 734
17 Liaw D-J, Liaw B-Y (1999) Polymer 40(11): 3183