

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Aromatic poly(amide-hydrazide)s: Synthesis and Characterization

V. P. Ubale^a; A. A. Ghanwat^b; P. P. Wadgaonkar^c; N. N. Maldar^b

^a D.B.F. Dayanand College of Arts and Science, Solapur, India ^b Department of Chemistry, Solapur University, Solapur, India ^c Division of Polymer Science and Engineering, National Chemical Laboratory, Pune, India

To cite this Article Ubale, V. P. , Ghanwat, A. A. , Wadgaonkar, P. P. and Maldar, N. N.(2009) 'Aromatic poly(amide-hydrazide)s: Synthesis and Characterization', Journal of Macromolecular Science, Part A, 46: 5, 541 — 546

To link to this Article: DOI: 10.1080/10601320902797830

URL: <http://dx.doi.org/10.1080/10601320902797830>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Aromatic poly(amide-hydrazide)s: Synthesis and Characterization

V. P. UBALE¹, A. A. GHANWAT², P. P. WADGAONKAR³ and N. N. MALDAR^{2,*}

¹*D.B.F. Dayanand College of Arts and Science, Solapur, 413 002, India*

²*Department of Chemistry, Solapur University, Solapur, 413 255, India*

³*Division of Polymer Science and Engineering, National Chemical Laboratory, Pune-8, India*

Received October 2008, Accepted November 2008

Aromatic poly(amide-hydrazide)s contain a higher percentage of polar group in the polymer backbone and represent a technologically important class of high performance material exhibiting high thermal, mechanical and chemical stability.

The present investigation deals with the synthesis of various new poly(amide-hydrazide)s and copolymers from new novel aromatic dicarboxylic acid i.e., 2,5-bis(4-carboxymethylene phenyl) 3,4-diphenyl thiophene (BCMPDT) and/or terephthalic acid with m-amino- and p-aminobenzhydrazide by Yamazaki's phosphorylation method. BCMPDT was characterized by spectroscopic techniques such as IR, NMR, and mass. Polymers were characterized by IR spectroscopy, solubility, inherent viscosity, thermal analysis (DSC, TGA), and X-ray diffraction studies.

These poly(amide-hydrazide)s had inherent viscosities in the range of 0.18–0.96 dL/g in DMSO at 30°C and showed good solubility in aprotic polar solvents. The polymers could be cast into transparent films and showed T_{max} in the range of 520–640°C. The structure property correlation for the series of poly(amide-hydrazide)s synthesized was studied in detail.

Keywords: 2,5-Bis(4-carboxymethylene phenyl) 3,4-diphenyl thiophene, poly(amide-hydrazide)s, Yamazaki's phosphorylation polycondensation, thermal properties

1 Introduction

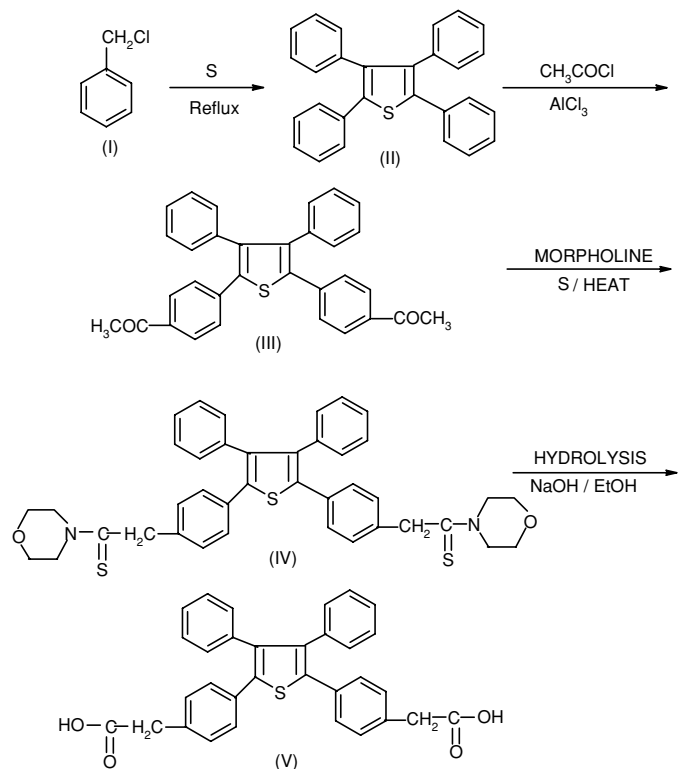
Aromatic polyamides and polyimides find applications as high performance materials. However, these are difficult to process into a desired shape because of their limited solubility in organic solvents; and high melting temperature and high glass transition temperature.

Copolymers such as poly(amide-hydrazide)s were expected to have better processing properties. Conventionally poly(amide-hydrazide)s were synthesized from dicarboxylic acid chloride and aminohydrazides such as p-aminobenzhydrazide, m-aminobenzhydrazide by the low temperature solution polycondensation method (1). To overcome the difficulties in handling moisture sensitive acid chloride, high molecular weight polyhydrazides and poly(amide-hydrazide)s were synthesized by Higashi-Yamazaki's phosphorylation method by direct polycondensation of an aromatic dicarboxylic acid in presence of

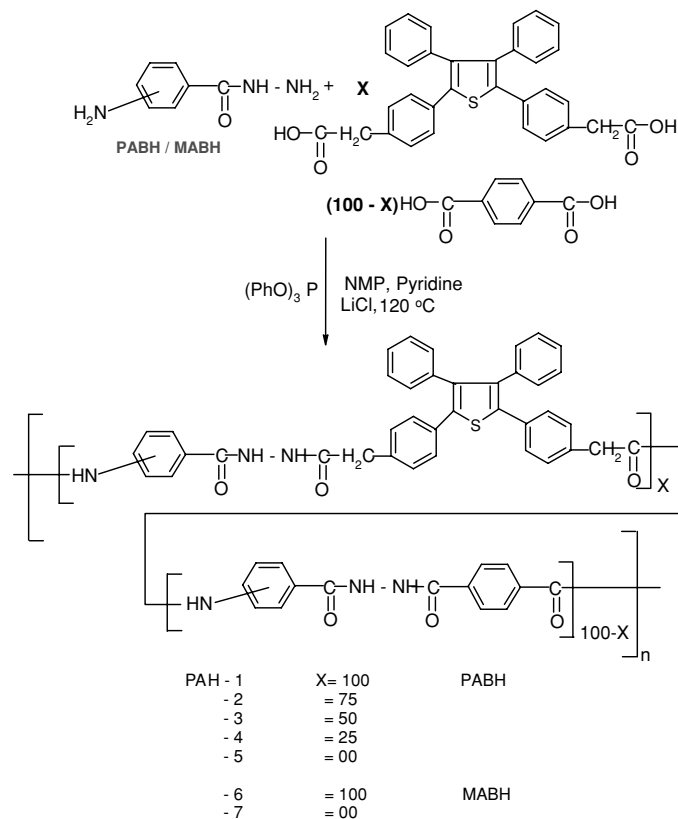
di- or tri-phenyl phosphite (2–7). Polyhydrazides and corresponding polyoxadiazoles containing furan moieties with improved properties were reported (8). In our earlier report, we have reported polyhydrazides from novel dicarboxylic acid 2,5-bis(4-carboxymethylene phenyl) 3,4-diphenyl thiophene and different dihydrazides by Yamazaki's direct phosphorylation method and studied the effect of incorporation of methylene group in polymer backbone (9). Aromatic poly(amide-hydrazide)s transition metal complex exhibited good solubility and easy processability into films and fibers and had better electrical conductivity (10–11). Aromatic poly(amide-hydrazide)s have high thermo-oxidative stability (12), and find use in reverse osmosis applications (13).

The present investigation reports the synthesis by Yamazaki's method; and characterization of soluble poly(amide-hydrazide)s and copolymers from novel dicarboxylic acid, 2,5-bis(4-carboxymethylene phenyl) 3,4-diphenyl thiophene (BCMPDT) (V); terephthalic acid and m-/p-aminobenzhydrazide. The structure property relationship; among a series of poly(amide-hydrazide)s and copolymers on basis of bulky pendant phenyl groups and flexible aliphatic units is discussed.

*Address correspondence to: N. N. Maldar, Department of Chemistry, Solapur University, Solapur, 413 255, India. E-mail: maldar_nn@rediffmail.com



Sch 1. Synthesis of 2,5-bis(4-carboxymethylene phenyl) 3,4-diphenyl thiophene (BCMPDT) (V):



Sch 2. Synthesis of poly(amide-hydrazide)s.

2 Experimental

2.1 Materials

N-Methyl pyrrolidone (NMP) was distilled under vacuum from calcium hydride before use and stored over 4A molecular sieves. Pyridine was refluxed over potassium hydroxide pellets under nitrogen, distilled and stored over 4A molecular sieves. Lithium chloride was dried under vacuum at 150°C for 6 h. p-Aminobenzoic acid, m-aminobenzoic acid, terephthalic acid were recrystallized by standard

procedures before use. Triphenyl phosphite (TPP) (Merck) was used after purification by distillation.

2.2 Measurements

Viscosity measurements were made with 0.5% (W/V) solution of polymers at 30°C using Ubbelohde suspended level viscometer. The solubility of polymers was determined at 3% concentration in various solvents at room temperature or by warming, if needed. The IR spectra of samples were recorded on a Perkin-Elmer 883 IR spectrometer as

Table 1. Synthesis^a of poly(amide-hydrazide)s and copoly(amide - hydrazide)s from (V).

Sr. No.	Polymer code	Diacid mol%		Aminohydrazide mol%		Yield (%)	Viscosity ^(b) η_{inh} (dL/g)
		V	TPA	PABH	MABH		
1	PAH-1	100	—	100	—	95	0.37
2	PAH-2	75	25	100	—	97	0.35
3	PAH-3	50	50	100	—	98	0.66
4	PAH-4	25	75	100	—	98	0.95
5	PAH-5	—	100	100	—	94	0.96
6	PAH-6	100	—	—	100	93	0.18
7	PAH-7	—	100	—	100	98	0.24

^aPolymerization was carried out with 1 mmol each of PABH/MABH and V/TPA.

^bMeasured at concentration of 0.5 g/dL in DMSO at 30°C.

Table 2. Solubility of poly(amide hydrazide)s:

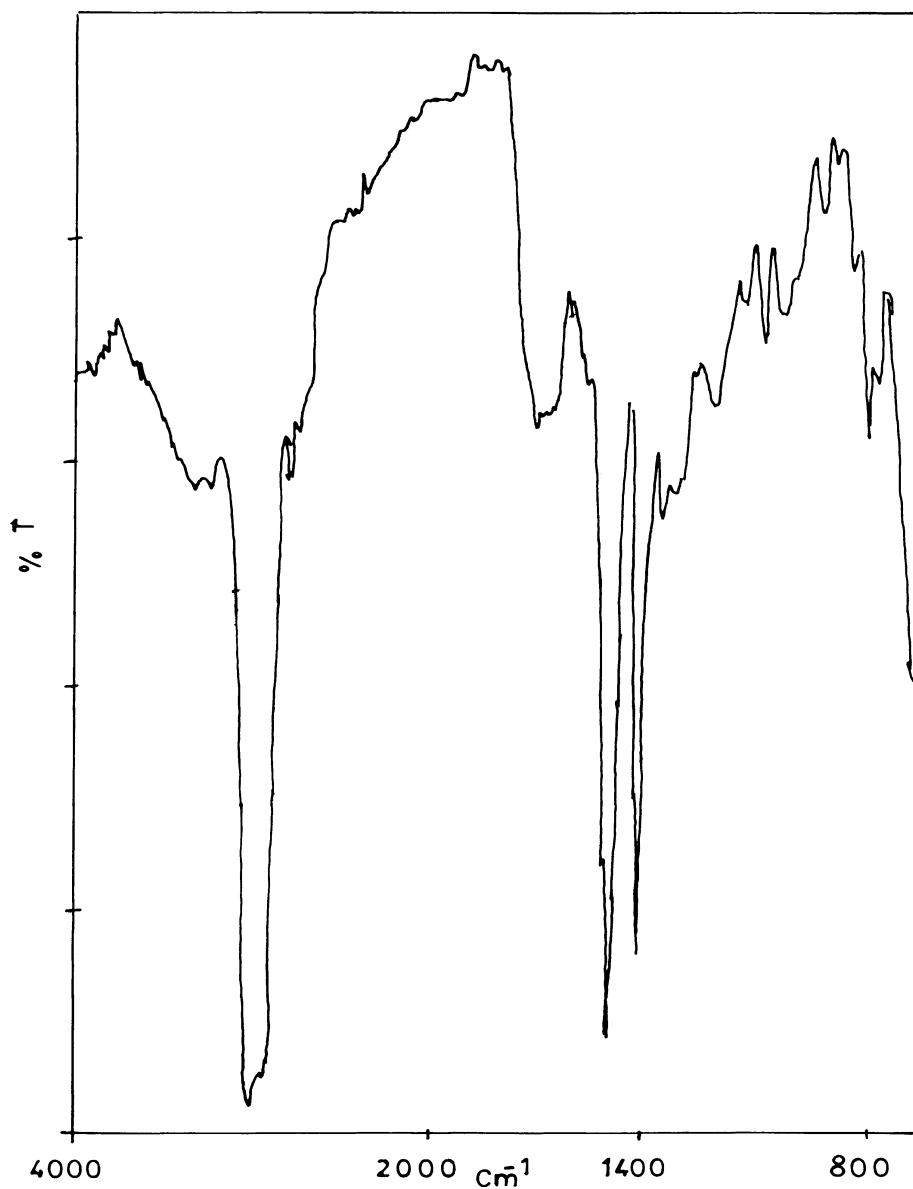
Solvent	Polymer						
	PAH-1	PAH-2	PAH-3	PAH-4	PAH-5	PAH-6	PAH-7
DMAc	++	++	++	++	+ -	++	++
DMSO	++	++	++	++	++	++	++
NMP	++	++	++	+	+ -	++	++
DMF	++	++	++	+ -	+ -	++	++
Pyridine	++	++	++	+ -	—	++	+ -
m- Cresol	++	++	++	+ -	—	++	+ -
HMPA	+	+	+	—	—	++	—
Conc. H ₂ SO ₄	++	++	++	++	++	++	++

++ Soluble at room temperature,

+ Soluble on heating,

+ - Partly soluble,

- Insoluble.

**Fig 1.** IR spectrum of PAH-3.

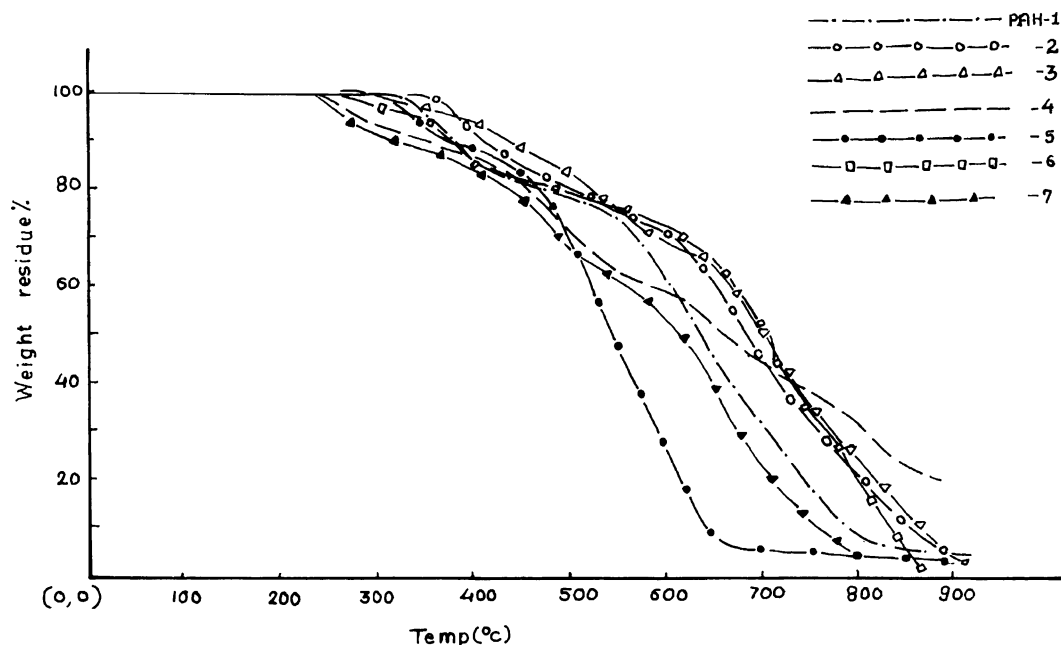


Fig 2. TG curves of PAH-1 to PAH-7.

KBr pellet or in nujol or as a polymer film. NMR spectra were recorded, on Varian T₈₀ MHz NMR spectrometer, whereas mass spectra were recorded on 11MS -30 double beam mass spectrometer. The thermogravimetry was performed on Rigaku Thermoflux TG- 8110 at a heating rate of 10°C/min under the nitrogen atmosphere.

2.3 Synthesis of Monomer

2,5-Bis(4-carboxymethylene phenyl) 3,4-diphenyl thiophene (V) was synthesized as reported by us earlier (14) (Scheme 1). m-Aminobenzhydrazide (MABH) and p-aminobenzhydrazide (PABH) were synthesized by the standard procedures.

2.4 Polymerization

By using the novel monomer 2,5-bis(4-carboxymethylene phenyl) 3,4-diphenyl thiophene (V) the poly(amide-hydrazide)s were prepared by Yamazaki's Phosphorylation method. (Scheme 2)

2.5 Synthesis of Poly(amide-hydrazide) (PAH-1)

In a 100 ml three-neck round bottom flask, equipped with magnetic stirrer, calcium chloride guard tube, reflux condenser and nitrogen gas inlet were placed 0.504 g (1 mmol) (V), 0.152 g (1 mmol) p-aminobenzhydrazide (PABH), 0.200 g lithium chloride (8 wt% based on solvent NMP and pyridine mixture) and 0.744 g (0.63 ml, 2.4 mmol) triphenyl phosphite (TPP), 0.5 ml pyridine and 2 ml NMP. The temperature of the reaction mixture was slowly raised

to 120°C with stirring over a period of 1 h, and heated at that temperature for 2 h under nitrogen. After cooling, the resulting viscous reaction mixture was poured into rapidly stirred 200 ml methanol, precipitated polymer was filtered and air-dried. The polymer was purified by dissolving in dimethyl sulphoxide (DMSO) and reprecipitated by methanol. It was filtered, washed with methanol and dried under vacuum at 100°C for 6 h. The yield was 95% and the inherent viscosity of polymer (PAH-1) in DMSO was 0.37 dL/g at 30°C.

All other poly(amide hydrazide)s i.e., PAH -2 to PAH -7 were prepared by a similar procedure.

Table 3. Thermal analysis data^(a) of poly (amide-hydrazide)s:

Polymer Code (deleted)	Temperature for various % Decomposition, °C			T _{max} ^(e) °C
	T _i ^(b)	T ₁₀ ^(c)	T ₅₀ ^(d)	
PAH-1	282	430	660	520
PAH-2	272	454	672	570
PAH-3	295	453	675	585
PAH-4	305	400	690	583
PAH-5	350	447	560	640
PAH-6	280	380	700	620
PAH-7	280	382	570	570

^aThermogravimetric analysis at heating rate of 10°C/min under nitrogen.

^bTemperature at which initial wt. loss observed.

^cTemperature at which 10% wt. loss observed.

^dTemperature at which 50% wt. loss observed.

^eTemperature of maximum rate of decomposition from DTG.

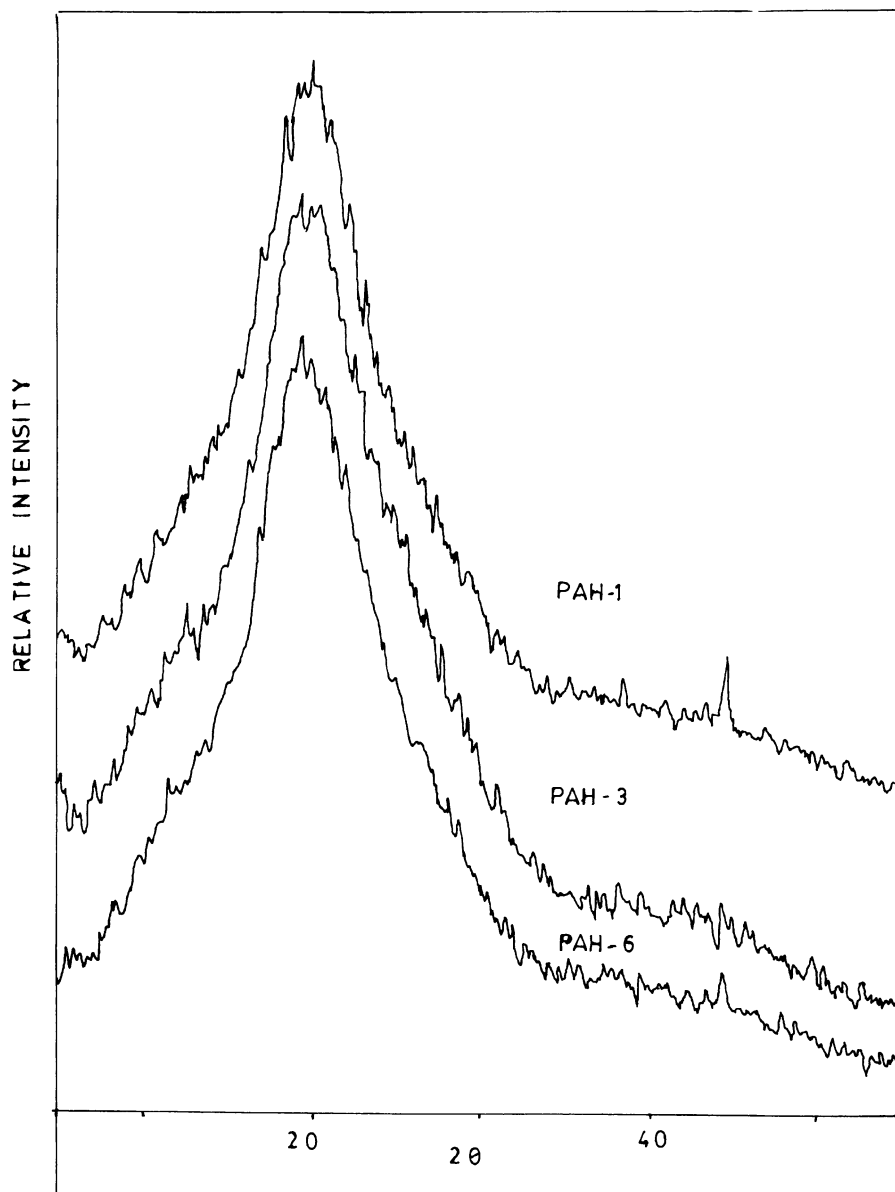


Fig 3. XRD curves of PAH-1, PAH-3 and PAH-6.

3 Results and Discussion

2,5-Bis(4-carboxymethylene phenyl) 3,4-diphenyl thiophene (V), was synthesized and characterized by IR, NMR and Mass spectroscopy.

In the present investigation, a series of poly (amide hydrazide)s and copolymers was synthesized by Yamazaki's phosphorylation polycondensation method; from (V), terephthalic acid with the *m*-aminobenzhydrazide (MABH)/*p*-aminobenzhydrazide (PABH) using triphenyl phosphite as a condensing agent. The polymerization was carried out in a mixture of NMP and pyridine (1:4 by volume) containing 8 wt% anhydrous lithium chloride at 120°C for 2 h under nitrogen.

Table 1 shows the data on the mol proportion of (V + TPA), yield and viscosities of the poly(amide-hydrazide)s. The polymers were obtained in quantitative yields, in the range 93 to 98%. The inherent viscosities of polymers were in the range of 0.18 to 0.96 dL/g; and they formed tough, flexible transparent films when cast from a polymer solution in DMSO. It was observed that polymers derived from MABH had lower viscosities (0.18–0.24 dL/g) than corresponding polymers based on PABH (0.35–0.96 dL/g); which may be assigned to the higher reactivity of PABH compared to the reactivity of MABH. Further among the polymers derived from PABH, the viscosity increased along the series (PAH-1 to PAH-5) as the mol% of TPA increased.

The poly(amide-hydrazide)s were also characterized by IR spectroscopy. The IR spectrum of polymer PAH-3 (Fig. 1) exhibited an absorption band at 3458 to 3051 cm^{-1} (N-H stretching) and at 1670 cm^{-1} (carbonyl stretching, amide-I).

The solubility characteristics of polymers are summarized in Table 2. All the polymers were soluble in DMSO, DMAc, NMP, conc. H_2SO_4 , (except PAH-5). Polymers were insoluble in common organic solvents such as chloroform, THF, methanol etc. It was observed that the polymers having more proportion of (V) (PAH-1 to PAH-3; PAH-6) had better solubility than the corresponding polymers derived from terephthalic acid (PAH-5 or PAH-7). As the proportion of terephthalic acid increased the solubility decreased. The better solubility of PAH-1, PAH-2, PAH-3 and PAH-7 was due to the bulky pendant phenyl groups and aliphatic spacer methylene linkage in the polymer backbone. Comparing the solubility of the polymers, PAH-1 and PAH-6; PAH-5 and PAH-7 indicated that polymers with meta- catenations (i.e. PAH-6, PAH-7) showed better solubility than corresponding PAH-1, PAH-5 having para-para linkages. Furthermore, this may be partly due to comparatively lower values of viscosities for PAH-6 and PAH-7.

The thermal stability of poly(amide-hydrazide)s was investigated by the thermogravimetry and the thermogravimetric curves/thermal stability data of polymers are shown in Figure 2 and Table 3, respectively. The thermograms show the weight loss 272°C onward, which can be assigned to the loss of water molecules because of the cyclodehydration of hydrazide moiety leading to formation of 1,3,4-oxadiazole rings. The subsequent curve indicates the degradation of the corresponding poly(amide-oxadiazole). The polymer showed T_{max} in between 520–640°C. T_{max} was found to increase (520–640°C) with an increase in the mol percentage of terephthalic acid unit in polymer as evidenced for PAH-1 to PAH-5.

The polymers were examined by means of wide-angle X-ray diffraction (WAXD) diagrams. As expected, due to the presence of higher mol percentage of bulky pendant groups; PAH-1, -3 and -6; showed an amorphous nature (Fig. 3).

4 Conclusions

A series of novel, new poly(amide-hydrazide)s and copolymers was synthesized from 2,5-bis(4-carboxymethylene phenyl) 3,4-diphenyl thiophene (V) along with different mol% of terephthalic acid and m-amino-/p-aminobenzhydrazide by direct polycondensation method using triphenyl phosphite as the condensing agent. These poly(amide-hydrazide)s had better solubility and the solubility improved as the mol proportions of (V) increased. This could be attributed to more amorphous nature of these polymers; as indicated by XRD; which is due to the presence of pendant phenyl moieties of the tetraphenyl thiophene units; and aliphatic methylene linkage in the polymers. Furthermore, m-catenated polymers PAH-6, PAH-7 showed better solubility than the corresponding p-catenated PAH-1, PAH-5 polymers. All these polymers showed good thermal stability.

References

1. Preston, J., Black, W.B. and Hofferbert, W.L. (1973) *J. Macromol. Sci. Chem.*, 7, 67.
2. Yamazaki, N., Masumoto, M. and Higashi, F. (1975) *J. Polym. Sci., Polym. Chem. Ed.*, 13, 1373.
3. Higashi, F., Akiyama, N. and Ogata, S. (1983) *J. Polym. Sci., Polym. Chem. Ed.*, 21, 913.
4. Higashi, F. and Ishikawa, M. (1980) *J. Polym. Sci., Polym. Chem. Ed.*, 18, 2905.
5. Ahraham, K.J. and Srinivasan, M. (1993) *Polym. International*, 32, 257.
6. Nakame, K. and Mohamed, N.A. (1993) *Polymer*, 34, 1310.
7. Shaikh, V.A.E., Ubale, V.P., Maldar, N.N., Lonikar, S.V., Rajan, C.R. and Ponratnam, S. (2006) *J. Appl. Polym. Sci.*, 100, 73.
8. Affi, A., Gharbi, S., Gharbi, R., Le, Bigot, Y. and Gandini, A. (2002) *Eur. Polym. J.*, 38, 667.
9. Ubale, V.P., Patil, A.S. and Maldar, N.N. (2007) *Eur. Polym. J.*, 43, 1038.
10. Qi, S.L., Wang, W.C., Wu, D.Z., Wu, Z.P. and Jin, R.G. (2006) *Eur. Polym. J.*, 42, 2023.
11. Mohamed, N.A. (2007) *Polymer Testing*, 26, 471.
12. Dovrnic, P.R. (1986) *J. Polym. Sci., Polym. Chem., Ed.*, 24, 1133.
13. Satre, M.D., Ghatge, N.D. and Ramani, P.M.S. (1990) *J. Appl. Polym. Sci.*, 41, 679.
14. Ubale, V.P., Sagar, A.D., Maldar, N.N. and Birajdar, M.V. (2001) *J. Appl. Polym. Sci.*, 79, 566.