

Synthesis and properties of poly(amide-imide-hydrazide)s and poly(amide-imide-1,3,4-oxadiazole)s

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Abstract. A series of new wholly aromatic and aromatic-aliphatic poly(amide-imide-hydrazide)s were prepared by the direct polycondensation from *p*-aminobenzhydrazide with various imide ring-containing dicarboxylic acids by means of diphenyl phosphite and pyridine. These polymers had inherent viscosities between 0.60 and 1.17 dl g⁻¹. Most of the poly(amide-imide-hydrazide)s were readily soluble in polar aprotic solvents such as N-methyl-2-pyrrolidone (NMP) and dimethyl sulfoxide (DMSO) and could be solution cast into light yellow, transparent, flexible, and tough films. These poly(amide-imide-hydrazide)s had T_g in the range 122–211 °C and could be thermally cyclodehydrated in the solid state to the corresponding poly(amide-imide-1,3,4-oxadiazole)s approximately in the range 250–400 °C, as evidenced by the differential scanning calorimetry thermograms. The thermally converted oxadiazole copolymers exhibited T_g in the range 120–271 °C and did not show significant weight loss before 380 °C in air or nitrogen. Effects of structural changes such as polymethylene length and the nature of the diacid monomers on the properties of polymers were studied.

1. Introduction

Aromatic polyimides are important classes of high-performance polymers due to their high thermo-oxidative stability, mechanical strength, and resistance to environmental degradation [1, 2]. However, rigidity of the backbone and charge transfer complex formation result in insolubility in most organic solvents and high softening temperatures. These properties make them generally difficult or too expensive to process, thus restricting their applications. Therefore, much work has been done to improve the processability of aromatic polyimides while maintaining their desirable properties. It is well known that the synthesis of poly(amide-imide)s and poly(ether-imide)s can offer a compromise between excellent thermal stability and processability [3–6].

Incorporation of the hydrazide group or both of the amide and hydrazide groups into the polyimide backbone is another method used to enhance the processability of the polyimides. The hydrazide groups in the main chain can also be further converted into the more chemically resistant and thermally stable oxadiazole structure by heating the polymer in the bulk or fibre form at an elevated temperature [7]. Poly(imide-1,3,4-oxadiazole)s and poly(amide-imide-1,3,4-oxadiazole)s with good solubility as well as desirable mechanical properties and thermal properties might be attained by incorporating varied aromatic structure with flexible linkages such as hexafluoroisopropylidene, ether, sulfone, and isopropylidene into the polymer backbones [8–10]. Poly(imide-1,3,4-oxadiazole)s can be readily prepared from

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oxadiazole-containing diamines with dianhydrides via the general two-step method used to prepare aromatic polyimides [11]. Another approach for the synthesis of poly(imide-oxadiazole)s is the cyclodehydration of the poly(imide-hydrazide)s [8–10], in which the intermediate poly(imide-hydrazide)s are prepared from imide-preformed diacid chlorides and an aromatic dihydrazide by the low-temperature polycondensation method. Recently, we found that high molecular weight poly(imide-hydrazide)s or poly(amide-imide-hydrazide)s could be readily prepared from the direct polycondensation of imide-containing dicarboxylic acids with an aromatic dihydrazide or amino hydrazide monomer using the Yamazaki–Higashi phosphorylation technique [12–15], which has been successfully applied in the poly(amide-imide) synthesis in this laboratory [16–18]. The direct polycondensation route avoids using moisture-sensitive acid chlorides and should be a more convenient method to prepare the imide-hydrazide and amide-imide-hydrazide copolymers. The present study describes the synthesis of a series of novel poly(amide-imide-hydrazide)s from trimellitic anhydride-based monoimide- or diimide-diacids with *p*-aminobenzhydrazide using the direct polycondensation method. Basic characterization of the poly(amide-imide-hydrazide)s and their thermally cyclodehydrated poly(amide-imide-1,3,4-oxadiazole)s is also investigated.

2. Experimental details

2.1. Materials

According to the method reported previously [16–18], imide-dicarboxylic acids **I**₁ (mp 268.8 °C, peak temperature of the melting endotherm on the differential scanning calorimetry (DSC) curve; H_f 197.7 J g⁻¹, heat of fusion), **I**₂ (mp 246.1 °C, H_f 232.8 J g⁻¹), **I**₃ (mp 226.8 °C, H_f 207.6 J g⁻¹), **I**₄ (mp 226.1 °C, H_f 182.7 J g⁻¹), **I**₅ (mp 206.9 °C, H_f 190.6 J g⁻¹), **I**₁₀ (mp 164.9 °C, H_f 166.4 J g⁻¹), and **I**₁₁ (mp 168.3 °C, H_f 182.8 J g⁻¹) were synthesized by condensation of trimellitic anhydride with ω -amino acids, H₂N(CH₂)_{*m*}COOH, containing different numbers of methylene unit, *m* = 1, 2, 3, 4, 5, 10, and 11. Bistrimellitides **II**_a (mp 387.5 °C, H_f 175.6 J g⁻¹), **II**_b (mp 367.7 °C, H_f 165.7 J g⁻¹), **II**_c (mp 362.6 °C, H_f 195.9 J g⁻¹), **II**_d (mp 322.0 °C, H_f 202.6 J g⁻¹), and **II**_e (mp 231.7 °C, H_f 126.3 J g⁻¹) were prepared by condensation from trimellitic anhydride with 4,4'-oxydianiline, 4,4'-methylenedianiline, 4,4'-methylenedicyclohexylamine, 1,6-hexamethylenediamine, and 1,10-diaminodecane, respectively. Commercially available anhydrous calcium chloride was dried under vacuum at 180 °C for 10 h. N-Methyl-2-pyrrolidone (NMP) and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. *p*-Aminobenzhydrazide (*p*-ABH) (TCI) and diphenyl phosphite (DPP) (Fluka) were used without further purification.

2.2. Preparation of poly(amide-imide-hydrazide)s

A typical procedure for the synthesis of poly(amide-imide-hydrazide) **III**₁ is as follows. In a 50 ml flask, a mixture of 0.4980 g (2 mmol) of imide-dicarboxylic acid **I**₁ (0.498 g), 0.3023 g (2 mmol) of *p*-aminobenzhydrazide, 0.5 g of calcium chloride, 5 ml of NMP, 2 ml of DPP, and 1 ml of pyridine was heated with stirring at 120 °C for about 3 h. The milky solution became gradually homogeneously transparent, leading to a clear, highly viscous polymer solution. After cooling, the viscous solution was poured slowly whilst stirring into 300 ml of methanol. The light yellow fibre-like precipitate formed was washed repeatedly with methanol and hot water, collected by filtration, and dried to give a quantitative yield of poly(amide-imide-hydrazide) **III**₁. The inherent viscosity of the polymer was 1.00 dl g⁻¹, measured in

DMAc-5 wt% LiCl at a concentration of 0.5 g dl⁻¹ at 30 °C. Elemental analysis: calculated for (C₁₈H₁₂N₄O₅)_n (360.28): C 59.34%; H 3.32%; N 15.38%; found: C 58.80%; H 3.35%; N 15.40%.

All other poly(amide-imide-hydrazide)s were synthesized by an analogous procedure.

2.3. Film preparation and cyclodehydration of the poly(amide-imide-hydrazide)s

A polymer solution was made by dissolving about 0.8 g of the poly(amide-imide-hydrazide) samples in 8 ml of N,N-dimethylacetamide (DMAc). The solution was poured into a flat glass culture dish, which was placed in a 90 °C oven for 12 h to remove the solvent. Then, the obtained semidried polymer film was lifted off the glass substrate and further dried in vacuum at 160 °C for 8 h. The obtained films had about 0.08 mm in thickness and were used for tensile testing and x-ray diffraction experiments.

The cyclodehydration of the poly(amide-imide-hydrazide)s to the corresponding poly(amide-imide-oxadiazole)s was carried out by heating the above fabricated polymer films at 150 °C for 30 min, 200 °C for 30 min, 250 °C for 30 min, and 300 °C for 1 h under a nitrogen atmosphere.

2.4. Measurements

IR spectra were recorded on a Jasco FT/IR-7000 spectrometer. Elemental analyses were run in a Perkin-Elmer model 2400 C-H-N analyser. ¹H NMR spectra were measured on a Jeol EX-400 NMR spectrometer. The inherent viscosities were measured with a Cannon-Fenske viscometer at 30 °C. A Perkin-Elmer DSC 7 differential scanning calorimeter equipped with a thermal analysis controller TAC 7/DX analyser was used to determine the thermal transitions. The heating rate was 20 °C min⁻¹ for normal scans and 5 °C min⁻¹ for the mp determination of the synthetic compounds. Glass transition temperatures (*T*_g) were read at the middle of the change in the heat capacity. Thermogravimetric analysis (TGA) was conducted with a DuPont 951 thermogravimetric analyser. Experiments were carried out on 9–12 mg samples heated in flowing nitrogen or air (50 cm³ min⁻¹) at a heating rate of 20 °C min⁻¹. Wide-angle x-ray diffraction measurements were performed at room temperature (about 25 °C) on a Siemens Kristalloflex D5000 x-ray diffractometer, using Ni-filtered Cu K_α radiation (40 kV, 20 mA). The scanning rate was 3° min⁻¹ over a range of 2θ = 5–45°. An Instron universal tester model 1130 with a load cell 5 kg was used to study the stress-strain behaviour of the samples. A gauge length of 2 cm and an elongation rate of 5 mm min⁻¹ were used for this study. Measurements were performed at room temperature with film specimens (6 cm long, 0.5 cm wide, and about 0.08 mm thick). Reported data are averages of at least five replica tests.

3. Results and discussion

3.1. Preparation of poly(amide-imide-hydrazide)s

The poly(amide-imide-hydrazide)s **III** and **IV** were prepared by direct polycondensation of *p*-aminobenzhydrazide (*p*-ABH) with imide-diacids **I** and **II** as shown in scheme 1, according to a modification of the Yamazaki-Higashi phosphorylation technique [12] developed by Preston and Hofferbert [13] for the synthesis of poly(amide-hydrazide)s. As demonstrated in our previous publication [19], more favourable results were obtained when using diphenyl phosphite (DPP) instead of triphenyl phosphite (TPP) in the phosphorylation polycondensation reactions between the dicarboxylic acid and dihydrazide or aminohydrazide monomers. Therefore, DPP was employed as a condensing agent in this study. The inherent viscosities

of the poly(amide-imide-hydrazide)s prepared are given in table 1. The inherent viscosity values ranging from 0.60 to 1.17 dl g⁻¹ are indicative of a moderate degree of polymerization. By using the reaction conditions listed in table 1, except for polymer **IV_c** all polymerizations proceeded homogeneously throughout the reaction and gave highly viscous polymer solutions. When pouring slowly into stirring methanol, the polymers were isolated as light yellow, tough, coiled threads. An early precipitation occurred during the propagation of poly(amide-imide-hydrazide) **IV_c**, and adding more solvent in order to carry out the reaction in a homogeneous phase has met with failure in producing a clear, viscous polymer solution. The less favourable result may be due to its lower solubility caused by a high level of crystallinity, as evidenced by x-ray diffraction experiments discussed subsequently. The cast film of polymer **IV_e** was highly brittle. This may also be explained by the higher crystallinity according to the x-ray diffraction patterns. The other poly(amide-imide-hydrazide)s afforded good-quality, flexible, and tough films by solvent casting, indicative of high molecular weight polymers.

Table 1. Synthesis conditions, inherent viscosities, and film quality of the poly(amide-imide-hydrazide)s.

Polymer code	Amounts of reagents used ^a			Remark ^b	η_{inh}^c (dl g ⁻¹)	Film quality ^d
	NMP (ml)	Py (ml)	CaCl ₂ (g)			
III₁	5	1	0.5	H	1.00	Flexible
III₂	5	1.2	0.5	H	1.17	Flexible
III₃	4	1	0.4	H	0.84	Flexible
III₄	5	1	0.5	H	0.69	Flexible
III₅	4	1	0.4	H	1.05	Flexible
III₁₀	5	1	0.5	H	0.75	Flexible
III₁₁	4	1	0.4	H	0.96	Flexible
IV_a	5	1	0.5	H	0.65	Flexible
IV_b	6	1.5	0.6	H	0.71	Flexible
IV_c	6 + 10	2	0.6	P	0.60	Insoluble
IV_d	7	1	0.7	H	0.89	Flexible
IV_e	6 + 5	1	0.6	H	0.60	Brittle

^a Reaction scale: 2 mmol of each monomer, DPP = 2 ml, reaction temperature = 120 °C, reaction time = 3 h.

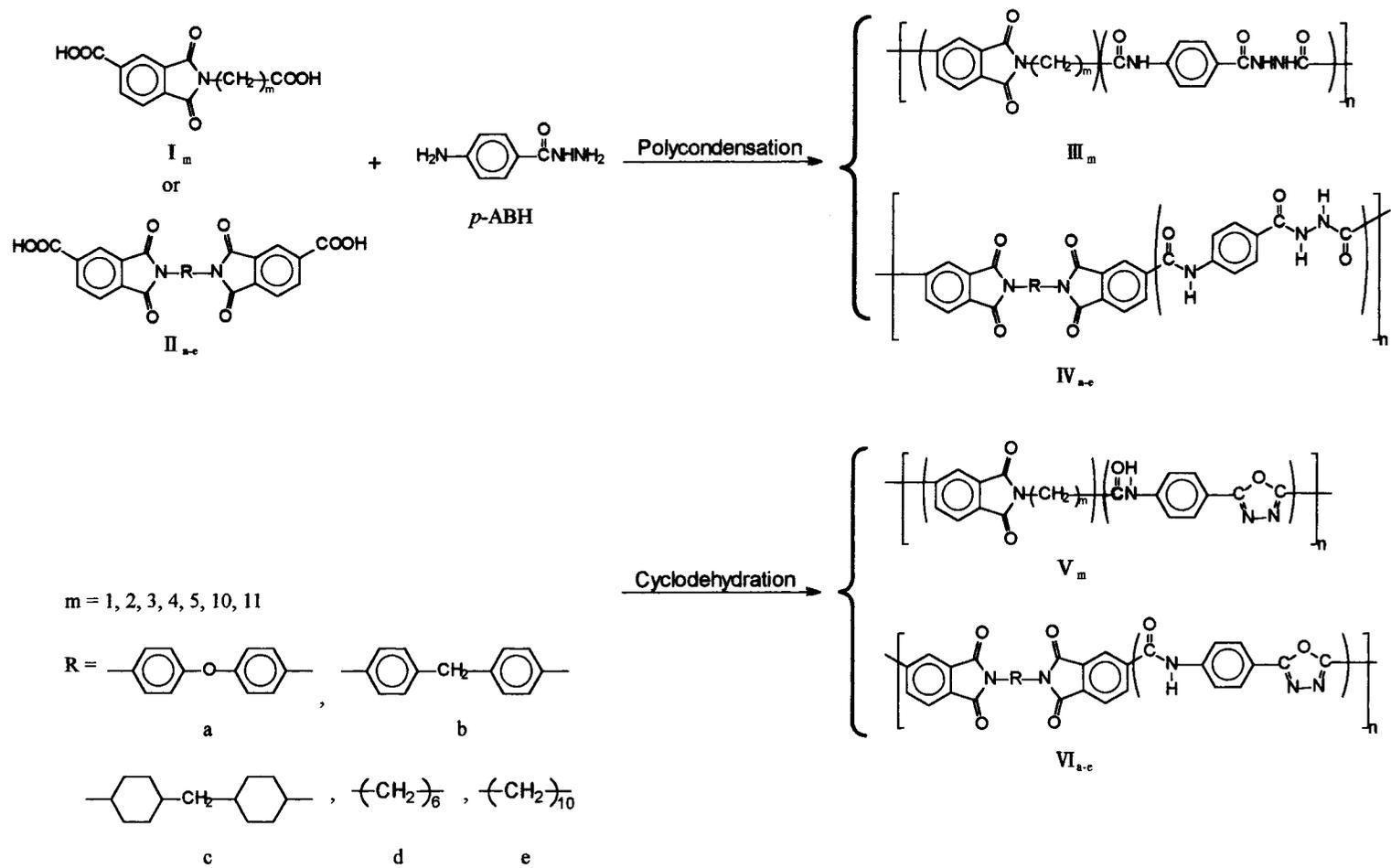
^b H: homogeneously transparent throughout the reaction, P: precipitation occurred during the reaction.

^c Measured at a concentration of 0.5 g dl⁻¹ in DMAc-5 wt% LiCl at 30 °C.

^d Films were cast from slow evaporation of the polymer solutions in DMAc.

3.2. Characterization of poly(amide-imide-hydrazide)s

Elemental analyses of the poly(amide-imide-hydrazide)s were generally in good agreement with their respective structures for hydrogen and nitrogen, while several of the carbon analyses were 1–2% below their theoretical values, a phenomenon common to high-temperature, heterocyclic polymers. The key structural features of the polymers synthesized were identified by FTIR spectroscopy. The IR spectra of all the poly(amide-imide-hydrazide)s exhibit absorptions characteristic of the hydrazide and amide groups near 3350 (N–H stretch) and 1650 cm⁻¹ (C=O stretch) and bands characteristic of the imide ring around 1780, 1720 (C=O stretch), 1390 (C–N stretch), 1100, and 720 cm⁻¹ (imide ring deformation). The molecular structures of the poly(amide-imide-hydrazide)s were also confirmed by solution NMR analysis. Figure 1 shows the ¹H NMR spectra measured in dimethyl-*d*₆ sulfoxide



Scheme 1.

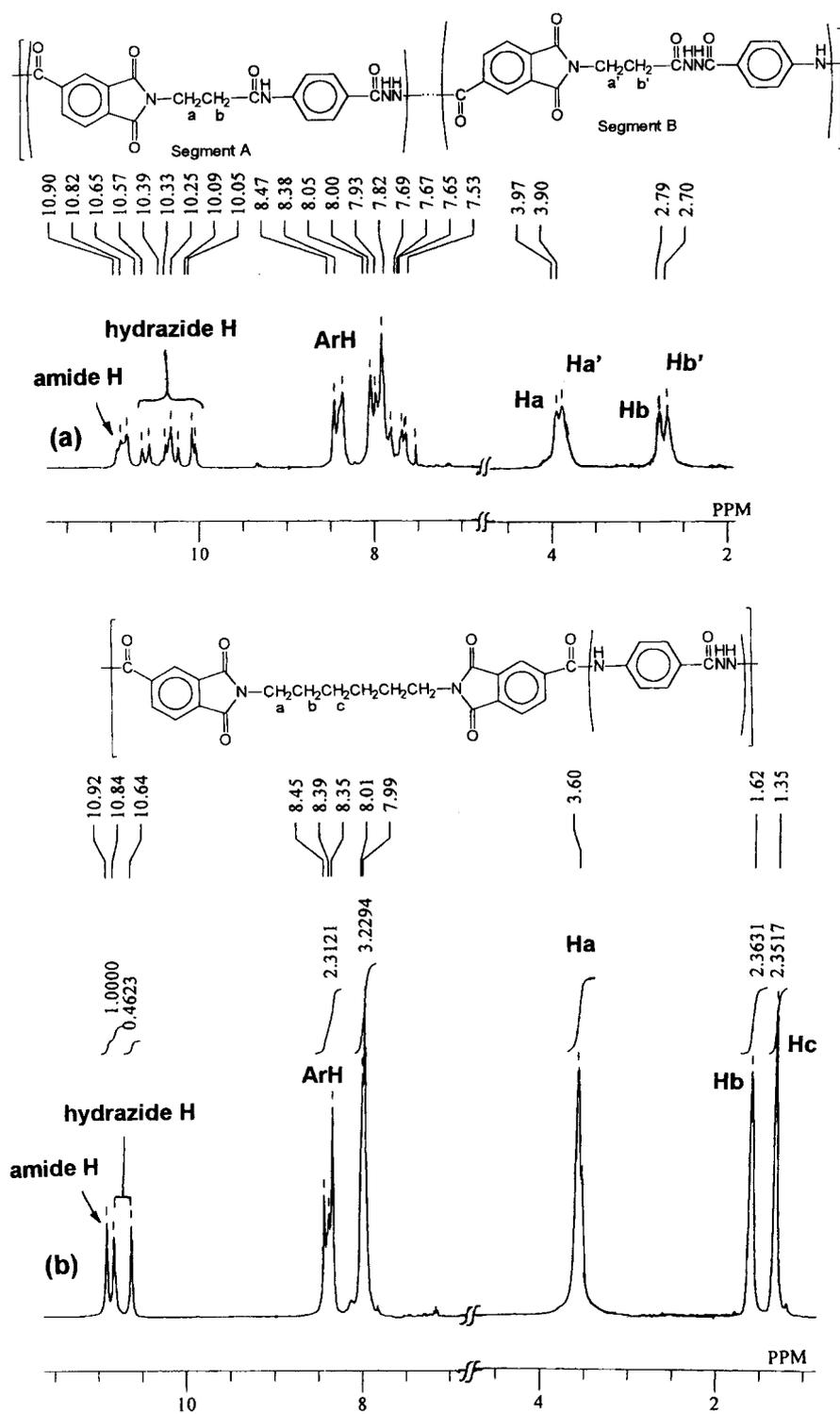


Figure 1. 400 MHz ^1H NMR ($\text{DMSO-}d_6$) spectra of poly(amide-imide-hydrazide)s (a) III₂ and (b) IV_d.

(DMSO- d_6) for the representative polymers **III**₂ and **IV**_d. In the spectrum of **III**₂, multiple resonances for the amide and hydrazide protons were observed between 10 and 11 ppm. This can be attributed to the constitutional disorder introduced by the asymmetric trimellitimide and *p*-ABH moieties, which give rise to a random enchainment of the repeat units. The same intensity of the methylene resonances suggests a statistical random distribution of head-to-head (such as segment A) and head-to-tail (such as segment B) linkages along the polymer backbone. Poly(amide-imide-hydrazide) **IV**_d gave a less complicated spectrum than **III**₂ because the former had a partially-ordered repeat unit.

The solubility of the poly(amide-imide-hydrazide)s was determined qualitatively in some common solvents at a concentration of 10 mg ml⁻¹, which is twice that used for measuring inherent viscosity. Table 2 summarizes the results of this study. Most poly(amide-imide-hydrazide)s are readily soluble in cold or hot polar solvents while insoluble in less efficient solvents. The relatively lesser solubility of polymer **IV**_c may indicate strong interchain interactions, such as hydrogen bonding between chains, or good packing ability due to the presence of the flexible cyclohexane ring.

Table 2. Solubility behaviour of poly(amide-imide-hydrazide)s. Solubility was tested qualitatively using 10 mg of sample and 1 ml of solvent.

Solvent	Polymer											
	III ₁	III ₂	III ₃	III ₄	III ₅	III ₁₀	III ₁₁	IV _a	IV _b	IV _c	IV _d	IV _e
NMP	+h	+	+	+	+	+	+	+h	+	—	+h	+
DMAc	+	+	+	+	+	+	+h	+h	+	—	+h	+
DMF	+	+	+	+	+	+h	+h	—	+	—	—	—
DMSO	+	+	+	+	+	+h	+h	+	+	—	+	+
<i>m</i> -Cresol	—	—	+h	+	+h	+h	+h	—	—	—	—	—
THF	—	—	—	—	—	—	—	—	—	—	—	—
Chloroform	—	—	—	—	—	—	—	—	—	—	—	—
Sulfolan	—	—	—	—	—	—	—	—	—	—	—	—
Ethanol	—	—	—	—	—	—	—	—	—	—	—	—

+, soluble at room temperature;
 +h, soluble on heating at 100 °C;
 —, insoluble even on heating.

The crystallinity of the poly(amide-imide-hydrazide)s was examined by wide-angle x-ray diffraction in film or powder samples. All the **III** series polymers could afford flexible films and revealed almost completely amorphous patterns due to their 'less ordered' backbone chains. For the 'partially ordered' poly(amide-imide-hydrazide)s **IV**_{a–e}, polymer **IV**_c showed a stronger reflection hump around $2\theta = 20^\circ$, indicating a higher packing density (figure 2). This result is consistent with its insolubility behaviour in organic solvents. Moreover, polymers **IV**_d and **IV**_e with a polymethylene unit between the trimellitimide segments also showed a similar, but less intense, reflection peak in the diffraction patterns. These results implied that those 'partially-ordered' poly(amide-imide-hydrazide)s with flexible aliphatic units in the chain backbone have higher crystallization tendency.

All poly(amide-imide-hydrazide)s except **IV**_c and **IV**_e could be solution cast into flexible films. These flexible films were subjected to tensile testing, and some tensile properties are listed in table 3. These films behaved as strong and tough materials. Most of them necked in tension and exhibited moderate extension to break. As shown in table 3, their tensile strengths, elongations at break, and initial moduli were recorded in the ranges 73–146 MPa, 12–76%, and 1.72–3.24 GPa, respectively.

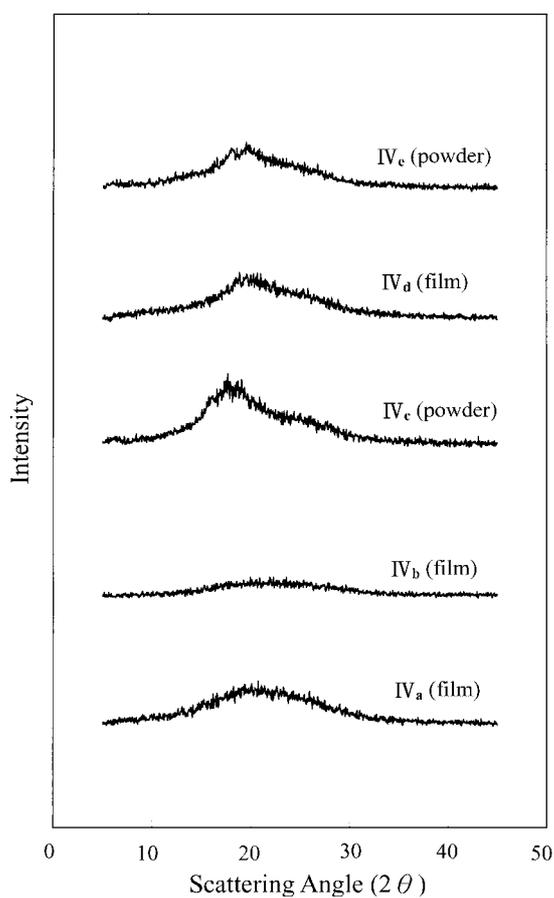


Figure 2. Wide-angle x-ray diffractograms of the poly(amide-imide-hydrazide)s **IV_{a-e}**.

Table 3. Tensile properties of poly(amide-imide-hydrazide) films.

Polymer Code	Tensile strength (MPa)	Elongation at break (%)	Initial modulus (GPa)
III₁	94	50	2.41
III₂	110	47	3.24
III₃	105	23	2.64
III₄	75	12	2.10
III₅	73	50	1.87
III₁₀	74	35	1.72
III₁₁	98	75	2.00
IV_a	146	53	3.09
IV_b	88	36	2.15
IV_d	91	76	2.51

Glass transition temperatures (T_g) of the poly(amide-imide-hydrazide)s were measured by DSC analysis. Because the absorbed moisture or the residual solvent and the history of thermal annealing may sometimes influence the first heating scan of DSC, samples were at first heated

to 200 °C at 20 °C min⁻¹, after which the samples were cooled down at a rate of -100 °C min⁻¹ to 30 °C, and the T_g was determined according to the second heating scan. All the poly(amide-imide-hydrazide)s except **IV_b** revealed clear glass transitions on their DSC traces, and the T_g values are summarized in table 4. Polymers of the **III** series had T_g between 122 and 196 °C, which were lowered with the increasing length of the methylene units. Poly(amide-imide-hydrazide)s **IV_{a-e}** had T_g in 146–211 °C range. Wholly aromatic **IV_a** exhibited a relatively higher T_g , and introduction of an aliphatic chain obviously decreased the T_g values.

Table 4. Thermal behaviour data of poly(amide-imide-hydrazide)s and poly(amide-imide-1,3,4-oxadiazole)s.

Poly(amide-imide-hydrazide)s ^a				Poly(amide-imide-oxadiazole)s				
Code	T_g (°C)	T_o (°C)	T_p (°C)	Code	T_d^c (°C)		Char yield ^d (%)	
					T_g^b (°C)	In N ₂		In air
III₁	196	312	335	V₁	256	445	437	54
III₂	178	280	340	V₂	242	396	395	52
III₃	136	272	302	V₃	214	448	444	65
III₄	131	279	308	V₄	243	432	430	59
III₅	131	267	296	V₅	189	450	452	60
III₁₀	123	257	281	V₁₀	131	452	452	41
III₁₁	122	251	269	V₁₁	120	450	454	38
IV_a	211	290	343	VI_a	261	515	526	61
IV_b	—	290	344	VI_b	271	515	517	67
IV_c	179	294	344	VI_c	210	465	455	38
IV_d	146	312	345	VI_d	175	470	472	49
IV_e	150	286	322	VI_e	155	457	459	45

^a DSC data obtained from the first DSC heating rate of 20 °C min⁻¹. T_g , midpoint of baseline shift on the DSC curve; T_o , extrapolated onset temperature of the endothermic peak; T_p , endothermic peak temperature.

^b Midpoint temperature of baseline shift on the second DSC heating trace of the sample after quenching from 400 °C.

^c Temperatures at which 10% weight loss was recorded by TGA at a heating rate of 20 °C min⁻¹.

^d Residual weight % when heated to 800 °C in nitrogen.

3.3. Cyclodehydration of poly(amide-imide-hydrazide)s

Cyclodehydration in the solid state has attracted much attention because of its simplicity and effectiveness [8]. The poly(amide-imide-hydrazide)s were cyclodehydrated into the corresponding poly(amide-imide-1,3,4-oxadiazole)s by heating them in film or powder form under nitrogen atmosphere according to the following curing cycle: 200 °C/30 min, 250 °C/30 min, and 300 °C/1 h. IR and NMR spectroscopy, thermogravimetric analysis (TGA), and DSC studied the cyclodehydration of these polymers. Thermal conversion of the hydrazide group to the 1,3,4-oxadiazole ring was monitored first by FTIR. As a representative study, a thin-film sample of poly(amide-imide-hydrazide) **IV_a** was heated sequentially under nitrogen atmosphere each for 30 min at 150, 200, 250, and 300 °C. The IR spectra of this sample are shown in figure 3. Cyclization of the hydrazide group to the oxadiazole ring occurred at 300 °C as seen by the decrease of the N–H stretching absorption around 3300 cm⁻¹ and the amide carbonyl peak at 1650–1660 cm⁻¹. The characteristic bands of the oxadiazole ring vibration at 1550–1570 cm⁻¹ reported in the literature [20–22] might be buried in the strong phenylene ring absorptions. Cyclization to the oxadiazole structure was also confirmed by ¹H NMR

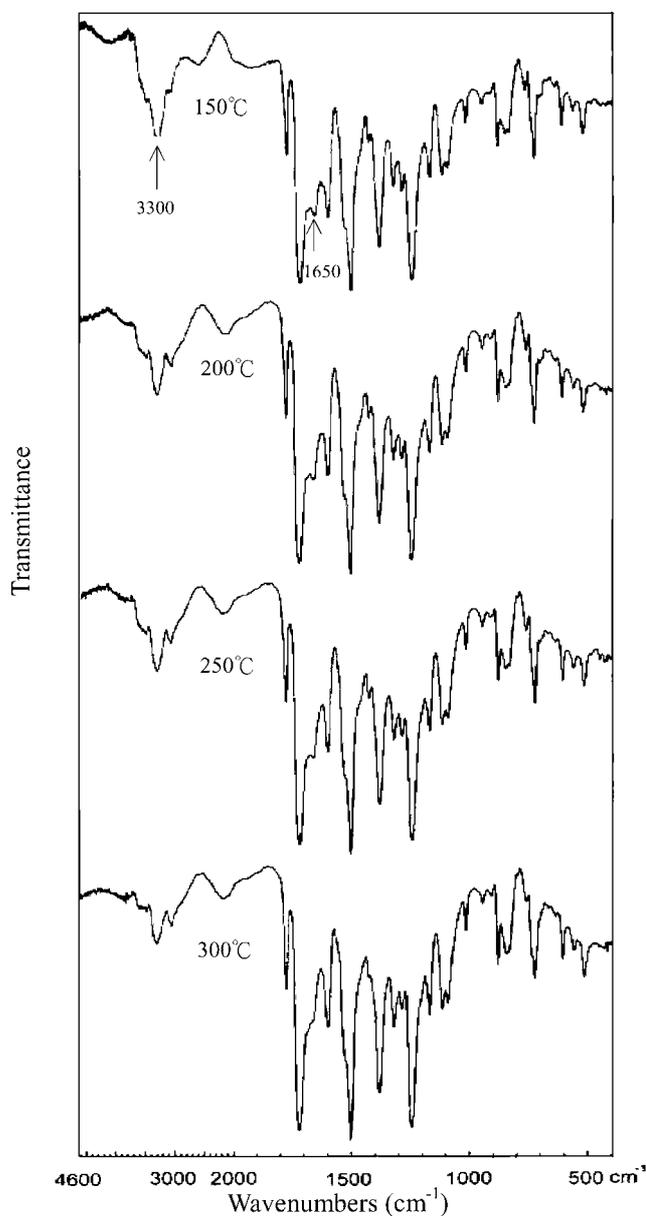


Figure 3. FTIR spectra (thin film) of poly(amide-imide-hydrazide) **IV**_a after sequential heating for 30 min at the indicated temperatures.

spectroscopy. Figure 4 illustrates the ¹H NMR spectra of poly(amide-imide-hydrazide) **III**₁ and its corresponding poly(amide-imide-1,3,4-oxadiazole) **V**₁. Polymer **III**₁ showed multiple hydrazide hydrogen peaks in the region 10.42–10.73 ppm. The NMR spectrum of the cyclized polymer **V**₁ did not show any peaks in this region, which indicates that cyclization is occurring to a high degree of conversion. In addition, the methylene hydrogens (H_b) of segment B in the polymer **V**₁ resonated at a lower field (5.18 ppm) due to the electron-withdrawing character of the oxadiazole unit. By TGA, the poly(amide-imide-hydrazide)s showed an initial weight

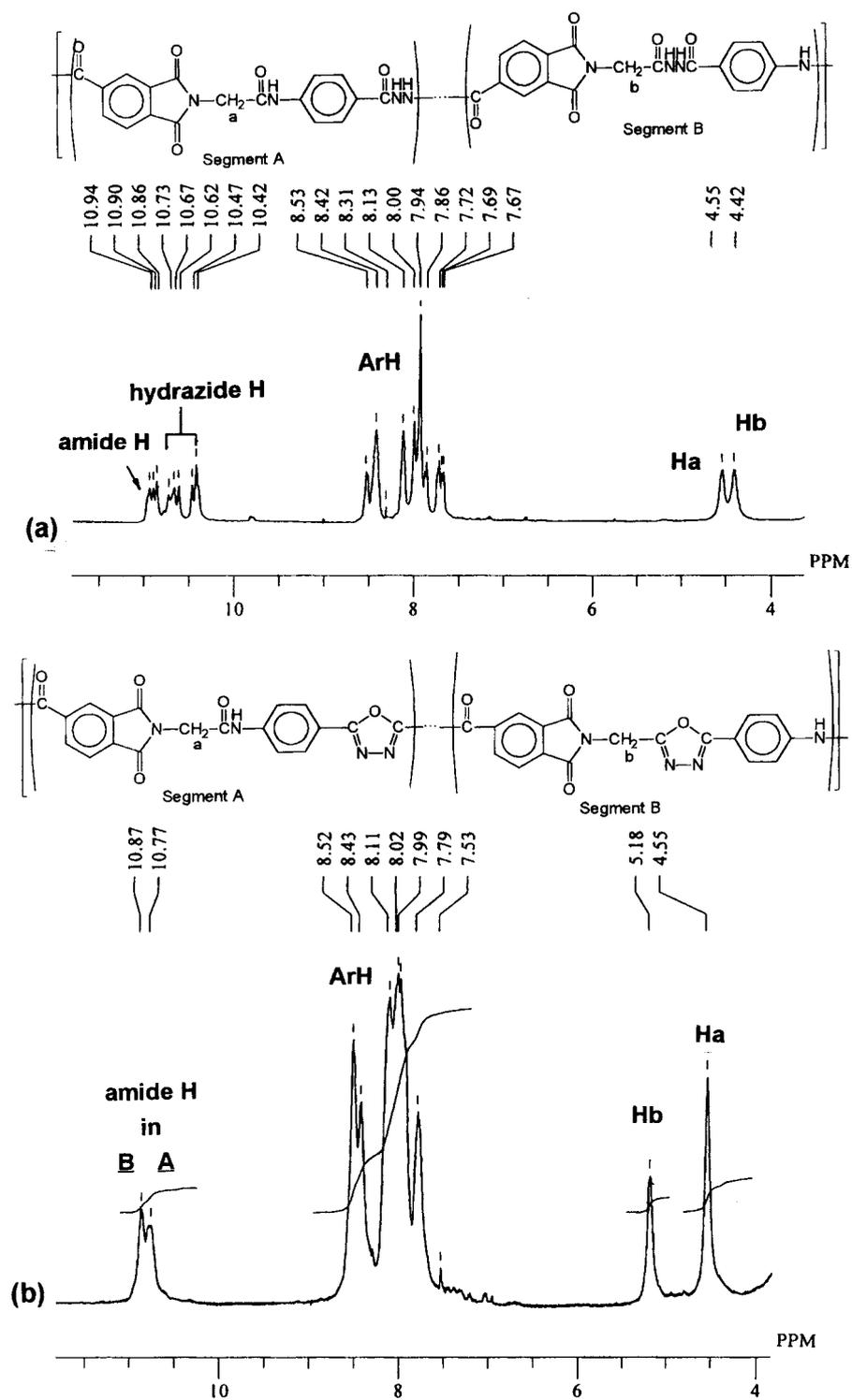


Figure 4. 400 MHz ¹H NMR (DMSO-*d*₆) spectra of (a) poly(amide-imide-hydrazide) III₁ and (b) poly(amide-imide-1,3,4-oxadiazole) V₁.

loss between 250 and 350 °C due to cyclodehydration of the hydrazide group to the 1,3,4-oxadiazole ring. This also agreed with the strong endothermic peaks observed in their DSC traces in a similar temperature range.

3.4. Properties of poly(amide-imide-1,3,4-oxadiazole)s

As described earlier, most of the poly(amide-imide-hydrazide)s prepared in this study were readily soluble in polar organic solvents and could be solution cast to transparent, light yellow, and tough films with good mechanical strengths. Thermal cyclodehydration in most cases resulted in shrunken and uncreasable poly(amide-imide-1,3,4-oxadiazole) films with a brownish or black colour and a decreased inherent viscosity, similar to those observed for polyoxadiazoles in the literature [20]. Stress build-up and chain shrinkage may have a deteriorating effect on the mechanical properties of these poly(amide-imide-1,3,4-oxadiazole) films. Among these poly(amide-imide-1,3,4-oxadiazole)s, only four of them such as **V**₅, **V**₁₁, **VI**_a, and **VI**_b gave flexible films. As shown in table 5, these thermally converted poly(amide-imide-1,3,4-oxadiazole)s had inherent viscosities between 0.23 and 0.77 dl g⁻¹, as measured in concentrated sulfuric acid. Most of them showed a dramatically decreased solubility, and, in fact, were insoluble in any available organic solvents. The ‘less-ordered’ polymers **V**_{1–3} with shorter methylene length were still soluble in cold or hot polar solvents.

Table 5. Inherent viscosities and solubility behaviour of poly(amide-imide-oxadiazole)s.

Polymer Code	η_{inh}^a (dl g ⁻¹)	Solvent ^b				
		NMP	DMAc	DMF	DMSO	<i>m</i> -cresol
V ₁	0.26	+	+	+h	+h	+h
V ₂	0.34	+	+h	—	+h	+h
V ₃	0.35	+	+h	—	+h	+h
V ₄	0.50	—	—	—	—	—
V ₅	0.62	—	—	—	—	—
V ₁₀	0.64	—	—	—	—	—
V ₁₁	0.77	—	—	—	—	—
VI _a	0.49	—	—	—	—	—
VI _b	0.45	—	—	—	—	—
VI _c	0.39	—	—	—	—	—
VI _d	0.61	—	—	—	—	—
VI _e	0.23	—	—	—	—	—

^a Measured in concentrated sulfuric acid at a concentration of 0.5 g dl⁻¹ at 30 °C.

^b Concentration: 10 mg/ml. +, soluble; +h, soluble on heating at 100 °C; —, insoluble even on heating.

Wide-angle x-ray diffractograms of poly(amide-imide-1,3,4-oxadiazole)s **VI**_{a–e} are shown in figure 5. All the **V** series polymers together with **VI**_a and **VI**_b, despite their more rigid molecular structure due to the presence of the oxadiazole ring, have almost no increased ordering as indicated by the x-ray diffractograms. However, the ‘partially-ordered’ poly(amide-imide-oxadiazole)s with flexible aliphatic segment, **VI**_{c–e}, displayed slightly enhanced crystallinity.

Thermal properties of the poly(amide-imide-oxadiazole)s were evaluated by DSC and TGA experiments, and their thermal behaviour data are included in table 4. These oxadiazole polymers exhibited T_g in the range 120–271 °C, which generally increased with decreasing chain flexibility. Due to the increased chain stiffness, almost all the oxadiazole polymers

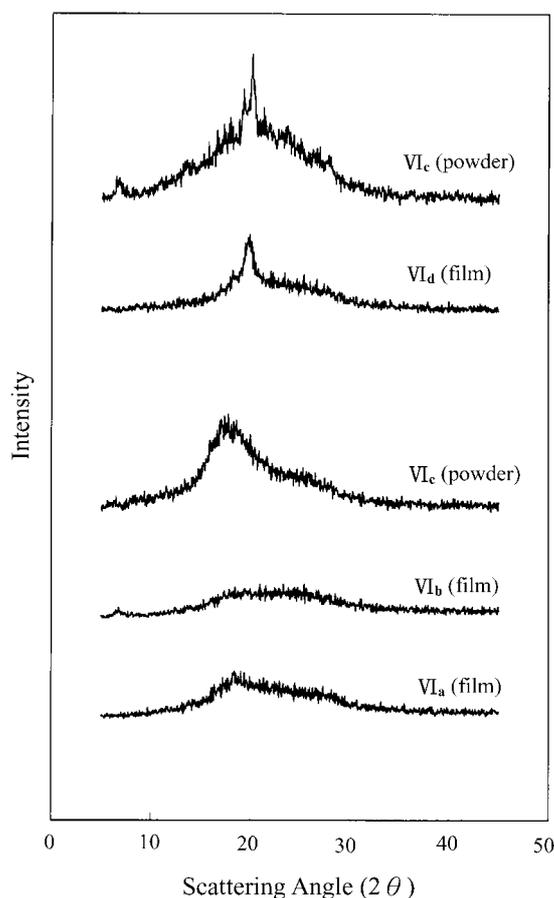


Figure 5. Wide-angle x-ray diffractograms of the poly(amide-imide-1,3,4-oxadiazole)s VI_{a-c} .

showed higher T_g values than the corresponding hydrazide precursor polymers. The wholly aromatic poly(amide-imide-oxadiazole)s VI_a and VI_b showed good thermal stability, with 10% weight loss temperature being recorded above 515 °C in air or nitrogen. As expected, the polymers containing aliphatic segments revealed a lower thermal stability; they began to decompose at about 380–400 °C.

4. Conclusions

High-molecular-weight poly(amide-imide-hydrazide)s were directly prepared from the N-(ω -carboxyalkyl)trimellitimides and bis(trimellitimide)s with *p*-aminobenzhydrazide by the phosphorylation reaction by means of diphenyl phosphite and pyridine in the NMP solution containing calcium chloride. The inherent viscosities of the polymers were in the range 0.60–1.17 dl g⁻¹, and most of them could be solution cast into light yellow and flexible films with good strengths and high toughness. The poly(amide-imide-hydrazide)s had T_g in the range 122–211 °C and could be thermally cyclodehydrated into the corresponding poly(amide-imide-1,3,4-oxadiazole)s at elevated temperatures. The oxadiazole polymers showed a significantly decreased solubility to organic solvents and higher T_g (120–271 °C) as compared

to the corresponding hydrazide precursors. Few poly(amide-imide-1,3,4-oxadiazole)s are organo-soluble and can afford flexible films. The wholly aromatic poly(amide-imide-1,3,4-oxadiazole)s showed good thermal stability, with 10% weight loss temperature being recorded above 500 °C in air or nitrogen atmosphere. Introduction of flexible aliphatic units in the polymer backbone resulted in a decrease in thermal stability and T_g and might lead to a higher packing density.

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