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Short communication

Synthesis, characterization and constitutional isomerism study of new aromatic polyamides containing pendant groups based on asymmetrically substituted *meta*-phenylene diamines

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ABSTRACT

Four new aromatic polyamides containing pendant groups were synthesized by low temperature interfacial polycondensation of two asymmetrically substituted diamine monomers, namely, 4-[4-(1-methyl-1-phenylethyl) phenoxy]-1,3-diamino benzene and 4-{4-[(4-methylphenyl) sulphonyl]phenoxy}-1,3-diamino benzene with two aromatic diacid chlorides, namely isophthaloyl chloride and terephthaloyl chloride. Inherent viscosities of polyamides were in the range 0.64–0.72 dL/g indicating formation of medium molecular weight polymers. The weight average molecular weights and number average molecular weights, determined by gel permeation chromatography (polystyrene standard), were in the range 54,500–65,000 and 19,750–27,000, respectively. The constitutional isomerism of synthesized polyamides was investigated by ^{1}H and ^{13}C NMR spectroscopy, where as the constitutional order was calculated from ^{1}H NMR spectroscopy and was found to be in the range 0.35–0.37. Polyamides containing pendant groups were essentially amorphous and were soluble in polar aprotic solvents such as *N*, *N*-dimethyl acetamide, *N*-methyl-2-pyrrolidone, *N*, *N*-dimethyl formamide and dimethyl sulfoxide. Polyamides exhibited glass-transition temperature in the range 237–254 °C. The initial decomposition temperature, determined by TGA in nitrogen atmosphere, of polyamides was in the range 371–410 °C indicating their good thermal stability.

1. Introduction

The chemistry of wholly aromatic polyamides has undergone outstanding developments in the last few years to overcome the problem of processability due to their high glass-transition and melting temperature [1,2]. Many novel diamine or diacid monomers have been specially designed using different approaches, such as incorporation of flexible or bridging functional groups [3–6], bulky pendant groups [7–11], cardo groups [12–14], heterocyclic rings [15,16] and *meta*- or *ortho*-catenated as a less symmetric aromatic units [17–19] to afford the success in preparation of organosoluble polyamides.

Most of the aromatic polyamides are prepared by reaction between two different bifunctional symmetric monomers, whereas polyamides from asymmetrically substituted *m*-phenylene diamine monomers (XabX) have been relatively less explored [20–23]. Polyamides based on asymmetrically substituted *m*-phenylene diamine monomers exhibit constitutional isomerism due to the unequal reactivities of functional groups in monomer units. The constitutional isomerism influences the cohesive energy of polyamides and, as a consequence, properties, such as glass-transition temperature (T_g), crystallinity, solubility and mechanical properties [23].

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The objective of this work was to synthesize new aromatic polyamides containing pendant groups based on two asymmetrically substituted *m*-phenylene diamine monomers namely, 4-[4-(1-methyl-1-phenylethyl) phenoxy]-1,3-diamino benzene and 4-{4-[(4-methylphenyl) sulphonyl]phenoxy}-1,3-diamino benzene by low temperature interfacial polycondensation with isophthaloyl chloride and terephthaloyl chloride. The resulting polyamides containing pendant groups were characterized by inherent viscosity measurements, gel permeation chromatography (GPC), solubility tests, IR, ^{1}H NMR and ^{13}C NMR spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) studies. The constitutional order of polyamides was determined with ^{1}H NMR spectroscopy.

2. Experimental

2.1. Materials

Terephthalic acid (S.D Fine, India), isophthalic acid (S.D. Fine, India) and thionyl chloride (S.D. Fine, India) were used without further purification. Terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) were synthesized by the reported procedures [24]. *N*, *N*-Dimethyl acetamide (DMAc; S.D. Fine, India) was purified by distillation under reduced pressure over calcium hydride and stored over molecular sieves 4 °A.

2.2. Monomer synthesis

4-[4-(1-Methyl-1-phenylethyl) phenoxy]-1,3-diamino benzene (**3a**) and 4-{4-[(4-methyl phenyl) sulphonyl]phenoxy}-1,3-diamino benzene (**3b**) were prepared as per procedure reported earlier from our laboratory [25].

2.3. Polyamide synthesis

Polyamides were synthesized by low temperature interfacial polycondensation technique [26]. A typical example of polymerization is described as follows: In a high speed stirring reactor were placed 4-[4-(1-methyl-1-phenylethyl) phenoxy]-1,3-diamino benzene (763 mg, 2.4 mmol), sodium carbonate (254 mg, 2.4 mmol) and distilled water (25 mL). The reaction mixture was cooled to 10 °C by an ice-bath. To the reaction mixture was added solution of isophthaloyl chloride (487 mg, 2.4 mmol) in dichloromethane (30 mL) in one lot, and the mixture was stirred rapidly for 30 min. The reaction mixture was poured into methanol (500 mL). The precipitated polymer was separated by filtration, washed with water, acetone, and methylene chloride. Polymer was dissolved in DMAc, the solution was filtered and filtrate was poured into methanol (600 mL). The fibrous polymer was filtered, washed thoroughly with methanol, acetone and methylene chloride and dried at 100 °C under vacuum for 12 h. All other polyamides were synthesized by similar procedure.

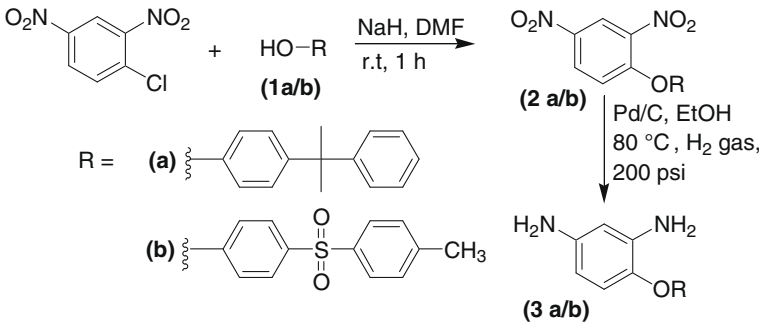
2.4. Measurements

Inherent viscosity measurements were made with 0.5% (w/v) solution of polyamides in DMAc at 30 ± 0.1 °C using an Ubbelhode suspended level viscometer. The weight average molecular weight (M_w) and number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polymers were measured with TOSOH HLC-8220 gel permeation chromatography (GPC) unit (eluent: DMF; calibration: polystyrene standards). IR spectra of polyamides were recorded on Perkin-Elmer 1600 FTIR spectrometer using KBr pellet technique. ^{1}H and ^{13}C NMR spectra of polymers were recorded on Bruker AMX-500 MHz spectrophotometer in DMSO-d_6. Wide angle X-ray diffraction (WAXD) measurements were made in the powder form of polyamides at room temperature on Jeol JDX-8030 X-ray diffractometer (operating at 30 kV and 30 mV) with nickel-filtered Cu K_α radiations (λ = 1.5418 °A). The scanning rate was 1.0 °/min over the range of 2θ = 10–50°. Thermogravimetric analyses of polyamides were made with NETZSCH 409 thermal analyzer. The measurements were recorded under N_2 atmosphere at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) analysis was performed on DSCQ100 V instrument at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Monomer synthesis

The synthesis of two diamine monomers, 4-[4-(1-methyl-1-phenylethyl) phenoxy]-1,3-diamino benzene (**3a**) and 4-{4-[(4-methylphenyl) sulphonyl]phenoxy}-1,3-diamino benzene (**3b**) was achieved in two steps according to the Scheme 1. The intermediate dinitro compounds, viz.



Scheme 1. Synthesis of asymmetrically substituted *meta*-phenylene diamines.

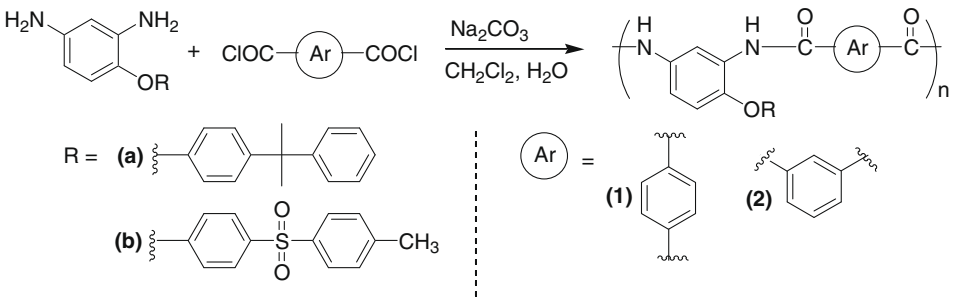
4-[4-(1-methyl-1-phenylethyl) phenoxy]-1,3-dinitro benzene (**2a**) and 4-{4-[(4-methylphenyl)-sulphonyl]phenoxy}-1,3-dinitro benzene (**2b**) were synthesized by aromatic nucleophilic displacement of 1-chloro-2,4-dinitro benzene with 4-(2-phenylisopropyl) phenol and 4-hydroxy-4′-methyl diphenylsulphone in the presence of NaH in DMF at room temperature. The diamine monomers (**3a/3b**) were obtained by the catalytic hydrogenation of dinitro compounds (**2a/b**).

3.2. Synthesis of polyamides and constitutional isomerism studies

Aromatic polyamides were synthesized by low temperature interfacial polycondensation of two asymmetrically substituted diamine monomers, namely, 4-[4-(1-methyl-1-phenylethyl) phenoxy]-1,3-diamino benzene and 4-{4-[(4-methylphenyl) sulphonyl]phenoxy}-1,3-diamino benzene with two aromatic diacid chlorides; namely isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC) (Scheme 2). The results of synthesis of polyamides are presented in Table 1. Polyamides were obtained in 98–99% yields and their inherent viscosity (η_{inh}) values were in the range 0.64–0.72 dL/g. To get information about the molecular weights achieved in the synthesis of these polyamides, measurements of the molecular weight were performed by gel permeation chromatography. Number-average molecular weights (M_n) were in the range 19,750–27,000, and weight average molecular weights (M_w) were in the range of 54,500–65,000. The molecular weight distribution for the polyamide samples which were isolated by precipitation method were in the range 2.65–2.75. Tough and transparent films of polyamides could be cast from their DMAc solution.

The formation of polyamides was confirmed by IR, ^{1}H NMR and ^{13}C NMR spectroscopy. IR spectra of polyamides PA-IIa and PA-IIb are shown in Fig. 1. IR spectra of polyamides exhibited characteristic absorption bands in the region 3400–3300 cm^{-1} (–NH stretching, broad band), 1665–1655 cm^{-1} (amide-I band, –C=O stretching, strong band), 1545–1520 cm^{-1} (amide-II band, interaction between –N–H deformation and –C–N stretching, strong band), 1248, 1050 cm^{-1} (–C–O–C– stretching, strong band) and IR spectra of polyamides synthesized from **3b** showed the additional absorption bands at 1340, 1130 cm^{-1} (–SO_2– stretching, strong band).

It was well reported [20] that when an asymmetric monomer reacts with symmetric monomer, constitutional isomerism would arise. Pino and coworkers [27] have reported a series of studies of the influence of constitutional isomerism on the physical properties of polycondensates, where the theoretical aspects of structural regularity of polycodensation were systematically investigated. They showed that the probability (s) of two adjacent



PA-Ia: R=a and Ar=1 **PA-IIa =R=a and Ar=2**

PA-Ib: R=b and Ar=1 **PA-IIb =R=b and Ar=2**

Scheme 2. Synthesis of aromatic polyamides containing pendant groups based on asymmetrically substituted *meta*-phenylene diamines.

Table 1
Yield, inherent viscosity, molecular weight, constitutional order, thermal properties and solubility of polyamides containing pendant groups.

Polyamides (PA)	η_{inh}[a] (dL/g)	M_w	M_n	M_w/M_n[b]	s[c]	T_g[d]	IDT[e] (°C)	Solubility[f]			
								DMAc	NMP	DMF	DMSO
Ia	0.68	60000	23500	2.70	0.37	254	410	+	+	+	++
IIa	0.72	65000	27000	2.75	0.35	240	395	+	+	+	+
Ib	0.65	56000	21050	2.71	0.36	250	400	+	+	+	+
IIb	0.64	54500	19750	2.65	0.35	237	371	+	+	+	+

[a] Measured at a concentration of 0.5 g/dL at 30 ± 0.1 °C in DMAc solvent.
[b] Determined from gel permeation chromatography (eluent: DMF; calibration: polystyrene standards).
[c] Determined by curve fitting method from ^{1}H NMR spectra of polyamides.
[d] Glass-transition temperature (T_g) measured on DSC at a heating rate of 10 °C/min.
[e] Initial decomposition temperature determined by TGA in nitrogen atmosphere.
[f] Solubility: (+) Soluble at room temperature; (++) soluble on heating.

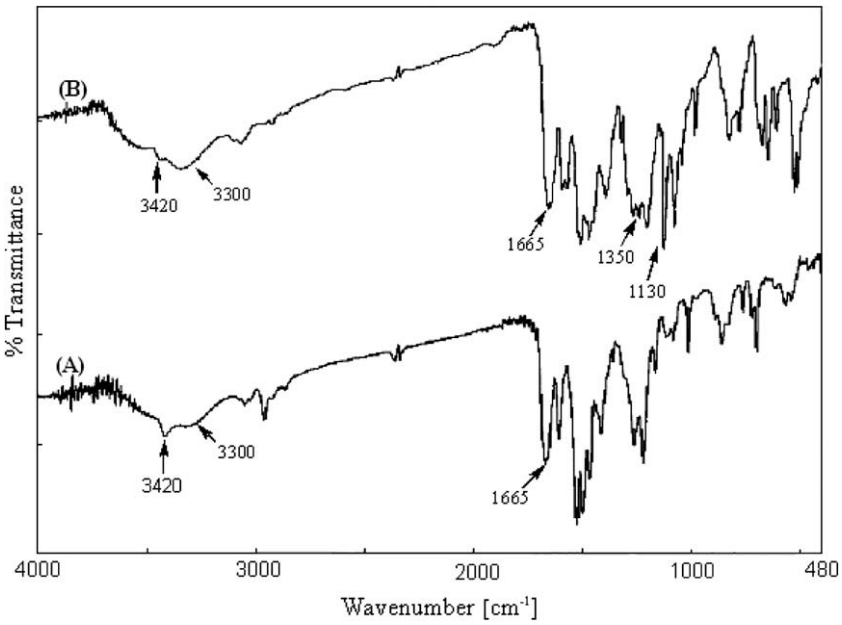


Fig. 1. FT-IR spectra of (A) PA-IIa and (B) PA-IIb in KBr.

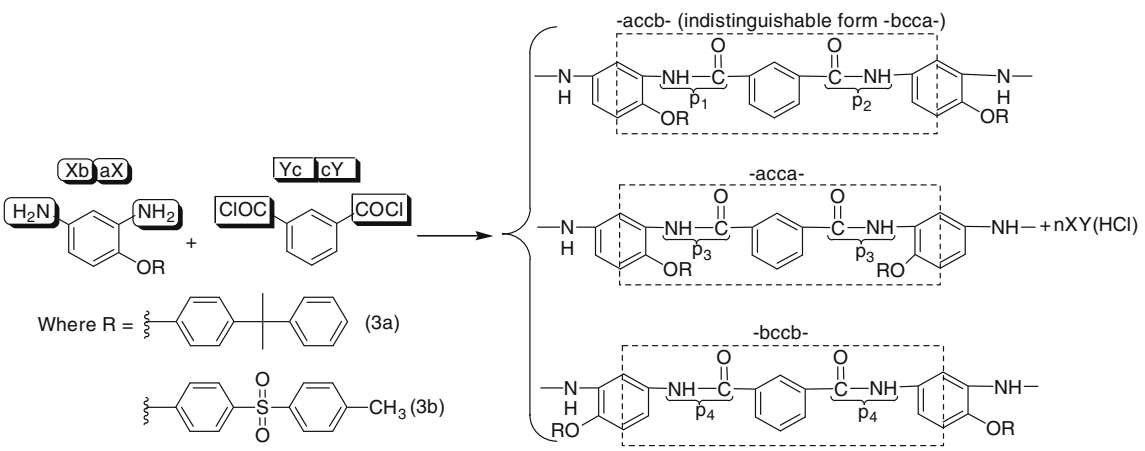
non-symmetric units in a chain pointing in the same direction could be used to quantify structural regularity. When an asymmetric monomer as **3a/3b** (XabX) is reacted with symmetric monomer TPC/IPC (YccY), the shortest structural elements in the polymers are -acca-, -accb-, -bcca- and -bccb-, where the two structures -accb- and -bcca- would be indistinguishable. The probability (s) of an element -accb- placement is given by equation 1, and the three general cases are shown in Scheme 3. For the chain where all units point in the same direction $s = 1$ (head-to-tail); when the orientation of the units is strictly alternating, $s = 0$ (head-to-head or tail-to-tail). If there were no constitution order, the polymer would be completely disordered.

$$s = \frac{[\text{accb}]}{([\text{acca}] + [\text{accb}] + [\text{bccb}])} \quad (1)$$

where

Brackets denotes molar concentration, and [accb] includes both -accb- and -bcca- arrangements.

^{1}H and ^{13}C NMR spectra of polyamides were consistent with their structure. As an example, ^{1}H and ^{13}C NMR spectrum of polyamide PA-IIa with expansion of aromatic region is shown in Figs. 2 and 3, respectively. A close scrutiny of the above spectrum revealed that two singlets were present at δ 1.60 and δ 1.58 corresponding to *gem*-dimethyl group. In addition, the amide regions of ^{1}H NMR spectra of polyamides PA-IIa and PA-IIb (Fig. 4) clearly showed the existence of constitutional isomerism. The presence of four different amidic protons peaks in the NMR spectra could be attributed to different structural elements -accb- (p_1), -bcca- (p_2), -acca- (p_3) and -bccb- (p_4) (Scheme 3). The peak assignment was made based on the



Scheme 3. Possible sequences in polyamide chain derived from asymmetrically substituted *meta*-phenylene diamines.

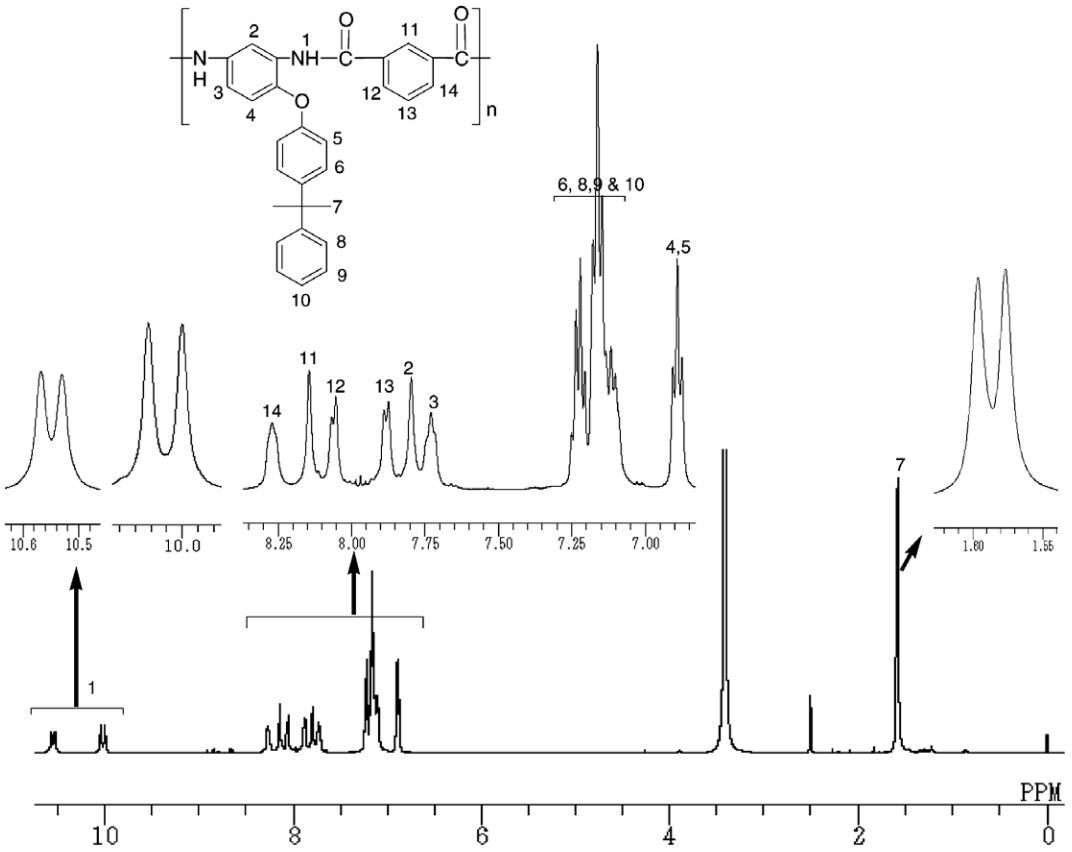


Fig. 2. ^{1}H NMR spectrum of PA-IIa in DMSO-d_6.

molecular modeling studies for different conformers of dimmer unit in the Gaussian program. The relative areas of each peak correspond to the molar ratio of the sequences and were determined by curve fitting. The value of probability factor (*s*) (Eq. (1)) was in the range 0.35–0.37 (Table 1). The near equal intensity of amide proton peaks in ^{1}H NMR spectra suggests a statistical random distribution of the asymmetrically substituted diamine moieties in the polymer chain. However, just by looking to the value of probability factor (*s*) and nature of ^{1}H NMR spectra, we can not claim completely that the synthesized polyamides are in random orientation because local order could still be present [21].

3.3. Properties of the polymers

Wide angle X-ray diffraction analysis of polyamides revealed that all the polyamides were amorphous in nature. The solubility behavior of polyamides containing pendant groups was tested qualitatively, and the results are included in Table 1. Polyamides dissolved readily at room temperature in polar solvents such as DMAc, *N*-methyl-2-pyrrolidone (NMP), *N*, *N*-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) except for PA-Ia, which required heating for dissolution in DMSO. The improved solubility of polyamides could be attributed to the cooperative effect of the weakening of intermolecular interactions due to the presence of bulky pendant groups and constitutional isomerism which results in to head-to-head, tail-to-tail and head-to-tail units in the main chain [23].

The thermal properties of polyamides were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TG curves of all polyamides showed more or less similar pattern of decomposition. The temperature characteristics, such as initial decomposition temperature (IDT), and glass-transition temperature (T_g) are given in Table 1. Polyamides exhibited T_g in the range 237–254 °C, depending on the structure of diamine and diacid chloride. As expected, TPC-based polyamides exhibited higher T_g values than corresponding polyamides based on IPC. The results of TGA analysis showed that the heat resistance temperature of polyamides varies in the range 371–410 °C (taking the sharp drop in the TG curve as marking the on set of decomposition) thus, indicating their good thermal stability.

4. Conclusions

Four new aromatic polyamides containing pendant groups were synthesized by low temperature interfacial polycondensation of two asymmetrically substituted diamine monomers with two aromatic diacid chlorides (TPC and IPC). Polyamides derived from asymmetrically

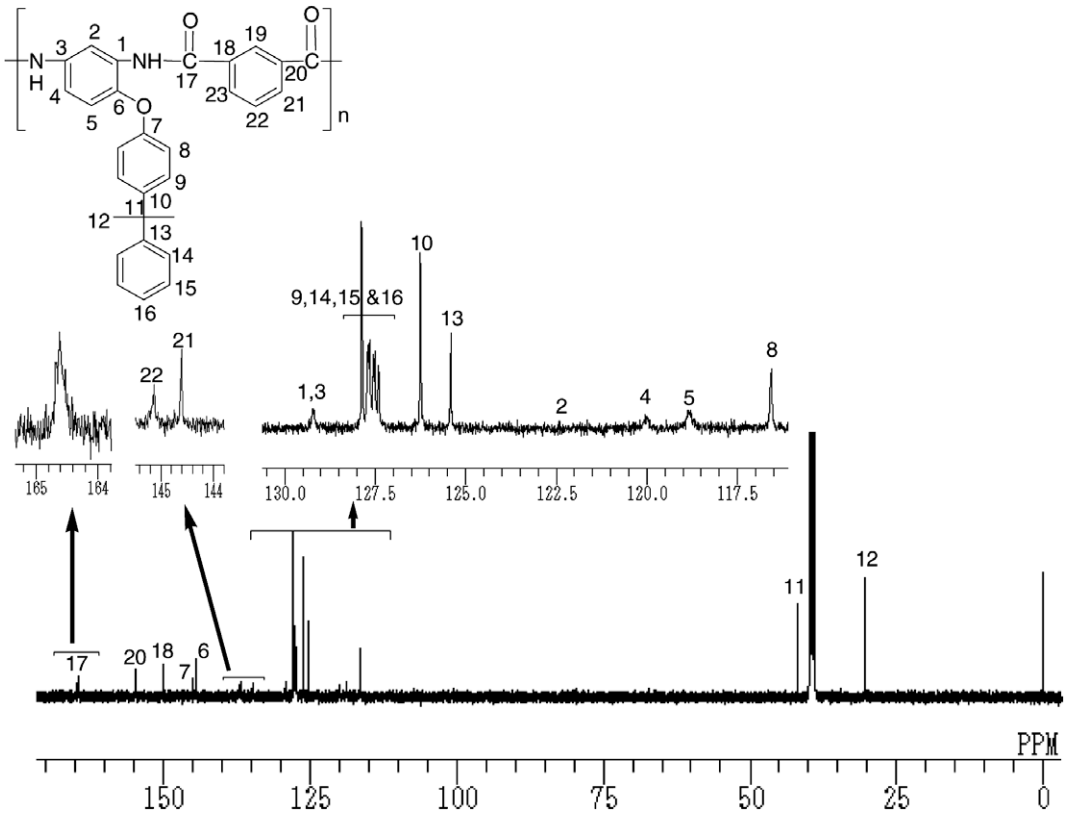


Fig. 3. ^{13}C NMR spectrum of PA-IIa in DMSo-d_6.

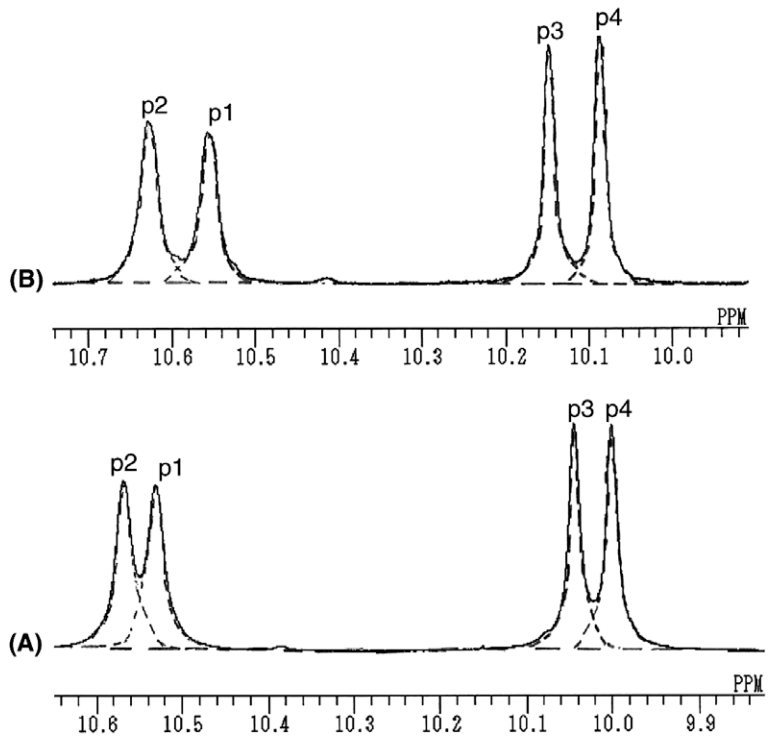


Fig. 4. Curve fitting (dash line) of ^{1}H NMR spectra (continuous line) of amide group region of polyamide (A) PA-IIa and (B) PA-IIb.

substituted *meta*-phenylene diamine monomers exhibited constitutional isomerism and the constitutional order in terms of the *s* parameter determined by ^{1}H NMR spectroscopy was in the range 0.35–0.37. Polyamides containing pendant groups were soluble in polar solvents such as NMP, DMAc and DMF and could be cast in to tough and transparent films from DMAc solution Polyamides exhibited glass-transition temperature in the range 237–254 °C. The initial decomposition temperature, determined by TGA in nitrogen atmosphere, of polyamides was in the range 371–410 °C indicating their good thermal stability.

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