

Synthesis and Properties of Novel Soluble Polychloro Substituted Aromatic Polyamides

Shou-Ri Sheng, Zhuo Liu, Xiao-Ling Liu, Yan Liu, Cai-Sheng Song

Department of Chemistry, College of Chemistry and Chemical Engineering, Jiangxi Normal University (YaoHu Campus), Nanchang 330022, People's Republic of China

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ABSTRACT: A novel monomer of tetrachloroterephthaloyl chloride (TCTPC) was prepared by the chlorination of terephthaloyl chloride catalyzed by ferric chloride at 175–180°C for 10 h, and confirmed by FTIR, MS, and elemental analysis. A series of new polychloro substituted polyamides with inherent viscosities of 1.17–1.28 dL/g have been prepared from TCTPC with various aromatic diamines. All the polyamides were amorphous and readily soluble in polar solvents such as NMP, DMAc, DMF, and DMSO at room temperature, and could afford flexible and tough films via solution casting. The cast films exhibited

good mechanical properties with tensile strengths of 83.6–106.8 MPa, elongations at breakage of 3.9–7.1%, and tensile modulus of 2.28–3.98 GPa. These polyamide films also exhibited good thermal stability with the glass transition temperature of 250–284°C, the temperature at 5% weight loss of 470–504°C and high char yields of 57.8–59.7% in nitrogen. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1112–1117, 2008

Key words: aromatic polyamides; polychloro-substituted; solubility; thermal properties; mechanical properties

INTRODUCTION

Aromatic polyamides (PAs) such as poly (1,4-phenylene terephthalamide) and poly (1,3-phenylene isophthalamide) are well known for their high-temperature stability, excellent mechanical strength, and good chemical resistance that qualify them as high-performance polymeric materials.^{1–5} Despite their outstanding properties, most of them have some drawbacks associated with infusibility and limited solubility in organic solvents, which were caused by the highly regular and rigid polymer backbones and the formation of intermolecular hydrogen bonding, resulting in their poor processability and restricting their applications. Therefore, much research effort has been directed at improving their processability without compromising their other desired properties. The strategies that have been employed to enhance the solubility of polyamides include the incorporation of flexible link-

ages,^{6–8} bulky pendent groups,^{9–11} unsymmetric,^{7,12–15} and alicyclic^{16,17} units into the polymer backbone. Although many excellent polyamides are known and commercially available, new polyamides are continuing to appear as researchers continue to conduct fundamental studies on chemical structure/property relationships. In this article, we describe the synthesis and characterization of a novel aromatic diacid chloride monomer, tetrachloroterephthaloyl chloride (TCTPC) (Scheme 1), and a series of the corresponding polyamides containing pendant polychloro groups (Scheme 2) derived from TCTPC with various aromatic diamines. The solubility, crystallinity, thermal, and mechanical properties for these new polymers were investigated.

EXPERIMENTAL

Materials

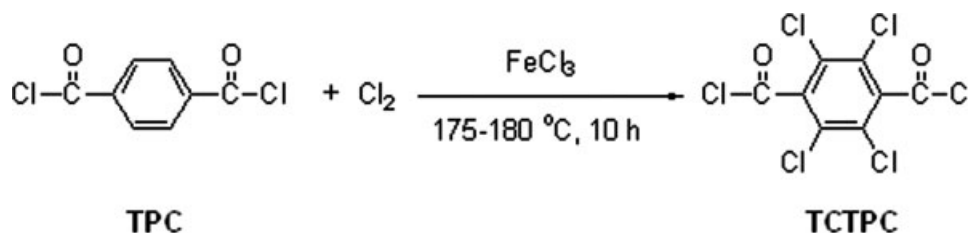
Terephthaloyl chloride (TPC), *N,N*-dimethylformamide (DMF), *N,N'*-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), chloroform, carbon tetrachloride, dichloromethane, methanol, toluene, anhydrous aluminum chloride, anhydrous ferric chloride, iron powder and calcium hydride were used as received. *N*-Methyl-2-pyrrolidone (NMP) was refluxed with calcium hydride and distilled under reduced pressure, then dried over molecular sieves 4 Å prior to use. *p*-Phenylenediamine (**2a**), *m*-phenylenediamine (**2b**) and 4,4'-oxydianiline (**2d**) were purified by vacuum sublimation.

Correspondence to: S.-R. Sheng (shengsr@jxnu.edu.cn).

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Scheme 1 Synthesis of TCTPC.

Benzidine (**2c**) and 1,4-bis(4-aminophenoxy)benzene (**2e**) were recrystallized from ethanol.

Monomer synthesis

TCTPC preparation

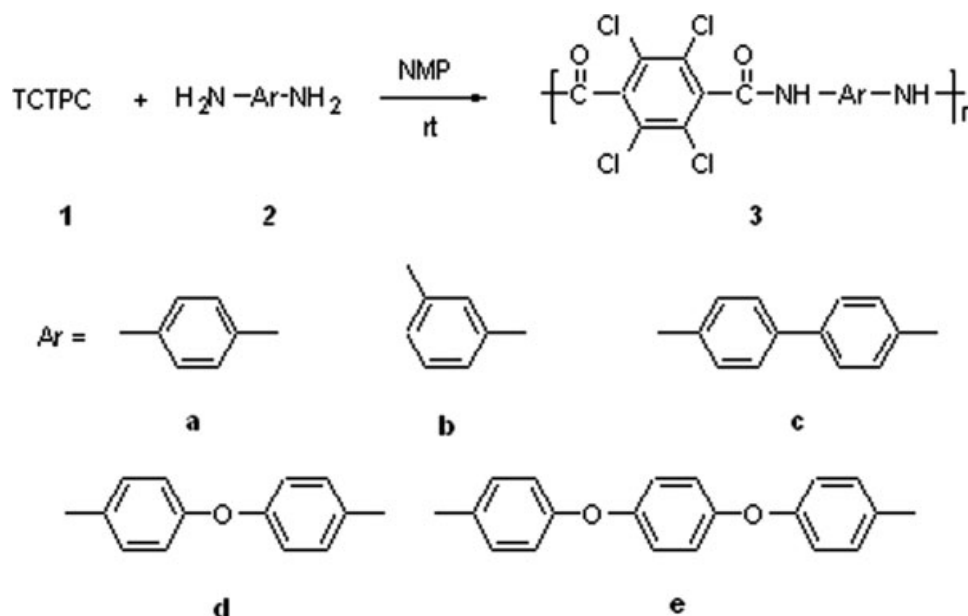
In a 100-mL three-necked flask equipped with a reflux condenser, magnetic stirrer, thermometer, and Cl_2 inlet was fitted with TPC (20.3 g, 0.10 mol), iron powder (0.28 g, 0.005 mol) and anhydrous FeCl_3 . The reaction mixture was placed in an oil bath preheated to 120°C , charged with dried Cl_2 maintained at 120°C for 2 h, and the temperature was then raised to $175\text{--}180^\circ\text{C}$ until the Cl_2 uptake ceased (generally 9–10 h). The hot reaction mixture was rapidly filtered, and the formed white precipitate was collected and recrystallized from carbon tetrachloride twice to afford 27.25 g (80% yield) of white crystals, m. p. $144\text{--}145^\circ\text{C}$. ^{13}C -NMR (CDCl_3): δ 162.9, 139.8, 128.3; EI-MS (70 eV): $m/z = 340$ (M^+ , 15.26), 342 (M^++2 , 12.46), 305 (100.00), 277 (59.47), 249 (22.36), 214 (23.64), 177 (23.31), 142 (47.66), 107 (36.28), 95 (8.48), 71 (21.04), 47 (15.61); FTIR: ν_{max} 1776, 1377, 1354, 1242, 1164, 945, 893, 743, 697, 589, 482 cm^{-1} .

Polymer synthesis

In a typical experiment, polyamide **PA-d**, which derived from TCTPC and 4,4'-oxydianiline (**2d**), was prepared as follows: **2d** (1.2014 g, 6.00 mmol) and pyridine (0.10 g) were dissolved in 40 mL of NMP, to which TCTPC (2.0447 g, 6.00 mmol) was added with stirring. The mixture was stirred in nitrogen at room temperature for 7 h to yield a viscous polyamide solution. Then the solution was trickled into excess ethanol with stirring to afford a precipitate. The precipitate was collected, washed with hot ethanol for three times and dried at 120°C under vacuum for 6 h to give polyamide **PA-d** (2.72 g, 97%). The other polyamides **PA-a**, **PA-b**, **PA-c**, and **PA-e** were also prepared via a similar procedure as described for **PA-d** by the polymerization of 1 equiv. of TCTPC with 1 equiv. of the corresponding aromatic diamines.

Preparation of polyamide films

The polyamide films were prepared via the casting of 15 wt % homogenous solution of the polychlorinated polyamide in DMAc into the clean glass plates, which



Scheme 2 Preparation of aromatic polyamides with pendant polychloro groups.

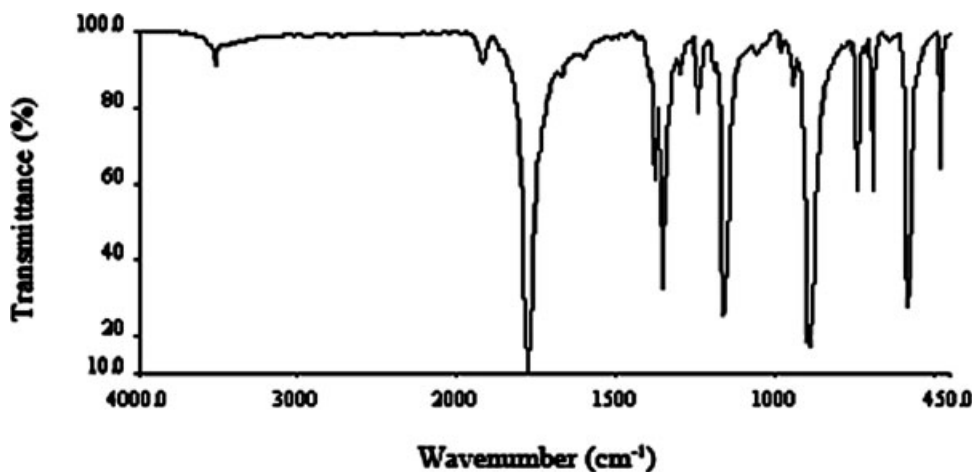


Figure 1 FTIR spectrum of TCTPC.

was placed in 90°C oven overnight for evaporation of the solvent. Then the obtained semi-dried polymer film was stripped from the glass plate and further dried in vacuum at 160°C for 6 h and 180°C for 1 h, successively. The obtained films with about 45- μm thickness were used for X-ray diffraction measurements, tensile tests, solubility tests, and thermal analyses.

Measurements

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were performed on a Bruker Avance 400 MHz spectrometer in CDCl_3 or $\text{DMSO-}d_6$. FTIR spectra were determined on a Perkin-Elmer SP One FTIR spectrophotometer. Mass spectra (EI, 70 eV) were recorded on a HP 5989B mass spectrometer. Microanalyses were performed with a PE 2400 elemental analyzer. The wide-angle X-ray diffraction measurements were recorded at room temperature (ca. 25°C) on power with a Rigaku Geiger Flex D-Max III X-ray diffractometer, using Ni-filtered $\text{CuK}\alpha$ radiation (operating at 40 kV and 15 mA); the scanning rate was 2°/min over a range of $2\theta = 2\text{--}40^\circ$. Differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) were recorded on a Perkin-Elmer 7 series thermal analysis system in nitrogen at a heating rate of 10°C/min. The mechanical properties were measured on an Instron 1122 testing instrument with $120 \times 5 \text{ mm}^2$ specimens in accordance with GB1040-79 at a drawing rate of 50 mm/min. Inherent viscosity was measured with an Ubbelohde viscometer with a 0.5 g/dL of polymer in NMP solution at $(25 \pm 0.1)^\circ\text{C}$, in which the polyamides were pretreated by drying in oven at 120°C for 1 h to remove the adsorbed moisture.

RESULTS AND DISCUSSION

Synthesis of TCTPC

The main aromatic diacid chloride monomer, TCTPC was prepared by the chlorination of commercially

available TPC at 175–180°C for 10 h in the presence of ferric chloride outlined in Scheme 1. To optimize crystallizing agents, several different solvents including *n*-hexane, petroleum ether, dichloromethane, benzene as well as carbon tetrachloride for purification of TCTPC were used. After a series of experiments, we found that carbon tetrachloride gave the best results. The structure of TCTPC was confirmed by mass spectrometry, FTIR, $^{13}\text{C-NMR}$ spectroscopy, and elemental analysis. In the IR spectroscopy (Fig. 1), TCTPC showed strong characteristic carbonyl absorption at 1776 cm^{-1} . Figure 2 shows the $^{13}\text{C-NMR}$ spectrum of TCTPC, in which all the carbons were assigned as expected.

Polymer synthesis

The polychloro substituted polyamides were prepared by a one-step pathway by polycondensation reaction of 1 equiv. of TCTPC and 1 equiv. of

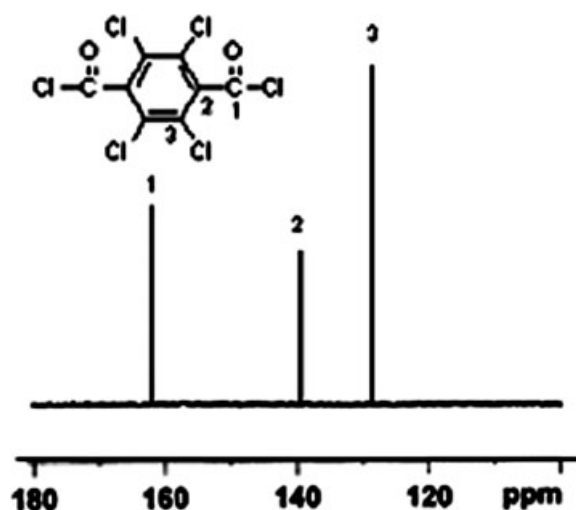


Figure 2 $^{13}\text{C-NMR}$ spectrum of TCTPC.

TABLE I
Preparation and Characterization of the Polymers

Polymer	Yield (%)	Elemental analysis ^a		η_{inh} (dL/g) ^b	T_g (°C)	T_d (°C) ^c	T_5 (°C) ^d	R_w (%) ^e
		C (%)	H (%)					
PA-a	97	44.78 (44.72)	1.72 (1.61)	1.20	265	448	490	59.6
PA-b	95	44.80 (44.72)	1.70 (1.61)	1.18	261	445	487	59.4
PA-c	97	53.24 (53.13)	2.29 (2.23)	1.17	284	454	504	59.7
PA-d	96	51.41 (51.32)	2.23 (2.15)	1.28	257	435	473	59.2
PA-e	97	55.82 (55.74)	2.64 (2.52)	1.23	250	434	470	57.8

^a Theoretical percentages are in parentheses.

^b Determined at 0.5 g/dL of polyamides in NMP at $(25 \pm 0.1)^\circ\text{C}$.

^c Onset decomposition temperature.

^d Decomposition temperatures at 5% weight loss in nitrogen.

^e Residual weight retention at 700°C in nitrogen.

aromatic diamine in NMP catalyzed by a trace of pyridine at 10 wt % of solid content (Scheme 2). A series of polychlorinated polyamides derived from TCTPC with various aromatic diamines (2a–2e) were prepared in good yields (95–97%). The physical properties and elemental analysis of these polyamides were listed in Table I. The resulting polyamides showed pale yellow colors, exhibited inherent viscosities of 1.17–1.28 dL/g in NMP at

25°C , implying that polymers have relative high molecular weights. The elemental analysis values were in good agreement with the calculated ones.

Structural features of these polyamides were confirmed by FTIR and $^1\text{H-NMR}$ spectroscopy. Figure 3 shows a typical $^1\text{H-NMR}$ spectrum for the polyamide PA-d, in which all the protons are in good agreement with the proposed structure. The resonance peaks appearing in the region of 10.61–10.75 ppm in the $^1\text{H-NMR}$ spectrum also support the formation of amide linkages. Figure 4 compares the FTIR spectra of all the resulting polyamides, which exhibited the characteristic absorptions of polyamides at $3320\text{--}3460\text{ cm}^{-1}$ (N–H stretching), $1670\text{--}1674\text{ cm}^{-1}$ (C=O stretching) and $1500\text{--}1550\text{ cm}^{-1}$ (combined N–H bending and C–N stretching), with strong absorptions of aryl ether group in the region of $1250\text{--}1260\text{ cm}^{-1}$. These results further demonstrated that the polychlorinated polyamides have the expected chemical structures.

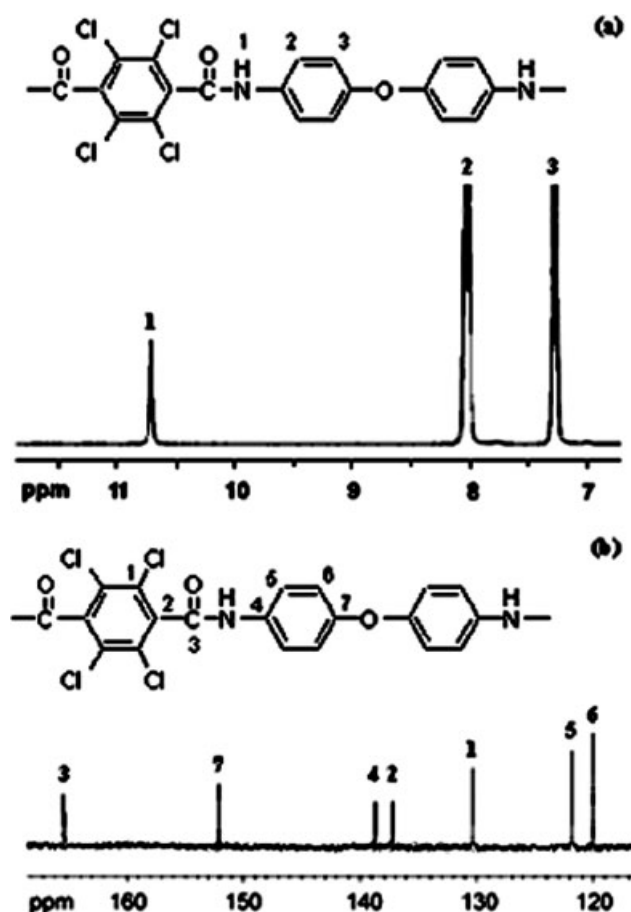


Figure 3 $^1\text{H-NMR}$ (a) and $^{13}\text{C-NMR}$ (b) spectra of the polyamide PA-d (DMSO- d_6).

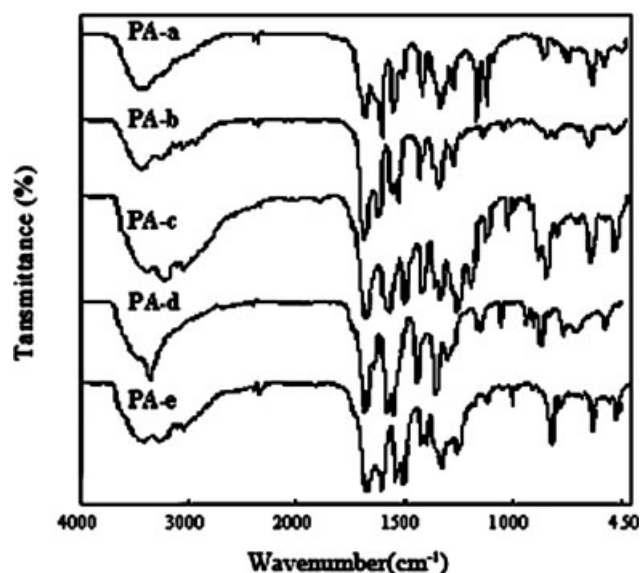


Figure 4 FTIR spectra of the polychlorinated polyamides.

Thermal stability

DSC and TGA were used to evaluate the thermal properties of these polychloro substituted polyamides. The thermal behavior data of the polymers are summarized in Table I. The glass transition temperature (T_g) values of these polyamides are in the range of 250–284°C. The high T_g s for the polymers might mainly result from the pendant polychloro substituents of monomers inhibiting the polymer backbone's free rotation. The polyamide **PA-d** exhibited the highest T_g value (284°C) because of the effect of the rigid biphenylene polymer backbone, whereas, the lowest T_g (250°C) was observed for polyamide **PA-e** derived from the multiring flexible diamine **2e**.

The thermal stability of these polyamides were measured by TGA. Figure 5 shows a typical TGA curve for the polyamide **PA-d**. It could be found that the polymer **PA-d** did not show obvious weight losses until the temperature reached 435°C in nitrogen, implying that no thermal decomposition occurred. However, as the temperature over 450°C, the polymer showed a rapid thermal decomposition. Seen from the Table I, these polymers have the onset decomposition temperatures in the range of 434–454°C, the temperatures at 5% weight loss in the range of 470–504°C. Compared to nonsubstituted wholly aromatic PAs, the incorporation of polychloro substituents produced a decrease in T_d in every case, but this effect did not deteriorate their thermal stability significantly. In addition, the anaerobic char yield at 700°C for all polymers was in the range of 57.8–59.7 wt % in nitrogen, which might have to do with the nature of the polychloro substituents and shows further good thermal stabilities of the polymers.

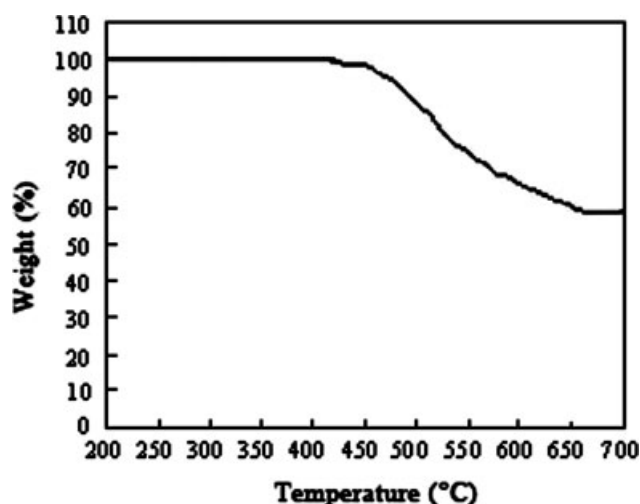


Figure 5 TGA curve of the **PA-d** in N_2 .

TABLE II
Solubility of the Polychlorinated Polyamides

	PA-a	PA-b	PA-c	PA-d	PA-e
NMP	++	++	++	++	++
DMSO	++	++	++	++	++
DMAc	++	++	++	++	++
DMF	++	++	++	++	++
<i>m</i> -Cresol	++	++		++	++
THF	–	–	–	–	+
$CHCl_3$	–	–	–	–	–
EtOH	–	–	–	–	–
Acetone	–	–	–	–	–

++, Soluble at room temperature in 2 h; +, soluble at room temperature in 24 h; –, insoluble.

Solubility

The solubility behavior of these polychlorinated polyamides was tested qualitatively by dissolving 1.5 g of polymers in 8.5 g of solvent (15 wt % of solid content) at room temperature, and the results are summarized in Table II. It can be seen that all the newly synthesized polyamides showed excellent solubility in aprotic polar solvents, such as NMP, DMAc, DMF, and DMSO. The good solubility of these polymers is apparently due to the presence of the pendant polychloro groups, which resulted in the decrease in the interaction of polymer chains by increasing the distance between polymer chains. The good solubility also makes these polyamides to be potential candidates for practical applications in spin-on and casting processes. On the other hand,

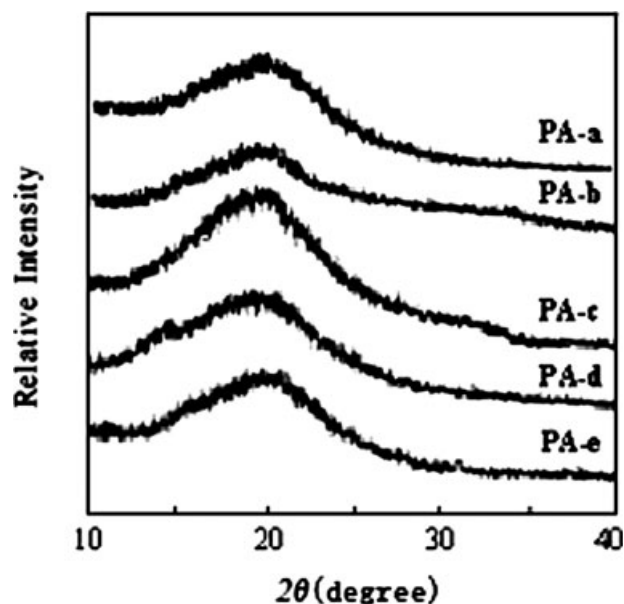


Figure 6 WAXD spectra of the polychlorinated polyamides.

TABLE III
Mechanical Properties of the Polychlorinated Polyamides

Polymer	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
PA-a	87.5	2.82	5.1
PA-b	85.8	2.78	4.9
PA-c	105.3	3.98	3.9
PA-d	106.8	3.31	7.1
PA-e	83.6	2.28	6.8

all the polymers except for polyamide **PA-c** are also soluble in *m*-cresol. **PA-c** was not soluble in *m*-cresol because of its rigid biphenylene segments in the polymer backbone. In addition, when comparing the other polyamides, it is found that polyamide **PA-e** exhibited better solubility because of the more flexible ether linkages on the polymer backbone. For example, **PA-e** could even be dissolved in THF at room temperature.

X-ray analysis

The WAXD patterns of the polychlorinated polyamides are shown in Figure 6. The results indicate that the polyamides are amorphous in nature. This can be attributable to the presence of polychloro pendant groups, which disrupted the regularity of molecular chains and inhibited the close packing of the polymer chains. Thus, the amorphous structure of these polymers also reflected in their good solubility and film forming ability.

Mechanical properties

All the polychlorinated polyamides could be processed into good-quality and flexible films. These films were subjected to tensile tests and their tests properties are listed in Table III. They showed good mechanical properties with tensile strengths, tensile modulus and elongation at breakage of these polyamide films were in the range of 83.6–106.8 MPa, 2.28–3.98 GPa and 3.9–7.1%, respectively, indicating strong and tough materials. Polyamide **PA-c**, which derived from benzidine, exhibited low elongation at breakage of 3.9%, due to the rigid polymer backbone. Polyamide **PA-d** based on TCTPC and 4,4'-oxydianiline (**2d**) showed the best mechanical prop-

erties, which might be attributed to the combined effect of the reaction activity of monomers and the flexible ether linkage in the polymer backbone.

CONCLUSIONS

A new monomer of TCTPC has been successfully synthesized and characterized from TPC, and then was used to polycondense with various aromatic diamines to form several novel polychloro substituted PAs. These polychloro substituted polyamides with high molecular weight exhibited high glass transition temperatures, good thermal stability and mechanical properties, as well as good solubility. These characteristics indicate that the polychlorinated groups in the polymer backbone have played an important role in the improvement of solubility and other properties of the polymer.

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