European Polymer Journal 38 (2002) 1721–1729

EUROPEAN POLYMER JOURNAL

www.elsevier.com/locate/europolj

New soluble poly(amide–imide–imide)s based on tetraimide-dicarboxylic acid condensed from 4,4′-oxydiphthalic anhydride, 2,2-bis[4-(4-aminophenoxy)phenyl]sulfone, and *p*-aminobenzoic acid, and various aromatic diamines

Chin-Ping Yang *, Ruei-Shin Chen, Chi-Shu Wei

Department of Chemical Engineering, Tatung University, 40 Chungshan North Road, Section 3, Taipei 104, Taiwan, ROC

Received 19 October 2001; received in revised form 2 January 2002; accepted 8 February 2002

Abstract

A new-type tetraimide-dicarboxylic acid (**I**) was synthesized starting from the ring-opening addition of *p*-aminobenzoic acid, 4,4′-oxydiphthalic anhydride, and 2,2-bis[4-(4-aminophenoxy)phenyl]sulfone (BAPS) at a 2:2:1 molar ratio in *N*-methyl-2-pyrrolidone (NMP), followed by cyclodehydration to the diacid **I**. A series of poly(amide–imide–imide)s ($\mathbf{III_{a-i}}$) with inherent viscosities of 0.71–0.99 dl/g was prepared by triphenyl phosphite-activated polycondensation from the tetraimide-diacid **I** with various aromatic diamines ($\mathbf{II_{a-i}}$) in a medium consisting of NMP, pyridine, and calcium chloride. All of the polymers were readily soluble in a variety of organic solvents such as NMP, *N*,*N*-dimethyl acetamide, dimethyl sulfoxide, and even in less polar *m*-cresol. Compared with those of the corresponding poly(amide–imide)s $\mathbf{IV_{a-i}}$, the solubilities of poly(amide–imide–imide)s $\mathbf{III_{a-i}}$ were greatly improved. Most of the polymers **III** afforded tough, transparent, and flexible films, which had a tensile strength ranging from 94 to 100 MPa, elongation at break from 7 to 9%, and initial tensile modulus from 2.0 to 2.3 GPa. The glass transition temperature of polymers was recorded at 265–291 °C. They had 10% weight loss at a temperature above 550 °C and left more than 50% residue even at 800 °C in nitrogen. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Tetraimide-dicarboxylic acid; Organosoluble poly(amide–imide–imide)s; Polycondensation

---

1. Introduction

Wholly aromatic polyamides belong to the class of high-performance polymers due to their high thermal and chemical resistance as well as high modulus [1,2]. Kevlar® [poly(*p*-phenylene)terephthalamide] and Nomex® [poly(*m*-phenylene)isophthalamide] are commercially marketed as high-performance polymers usually in fiber form. Most polyamides exhibit excellent tensile strength and thermal stability and are widely used for a variety of applications [1–5]. Aromatic polyimides are possessed of outstanding thermal behavior and noted for their excellent physical and electrical/insulating properties [1,3]. However, polyimides are difficult to process due to their high softening or melting temperatures and their insoluble nature. To overcome this drawback, various copolymers have been developed and reported [6–12], among them being poly(amide–imide)s, whose amide groups can improve the solubility.

Poly(amide–imide)s usually have been synthesized through three main routes. The first route goes through the amide–imide-forming reaction, by which trimellitic anhydride (TMA) reacts either with diisocyanate to produce poly(amide–imide) [13–16] or with thionyl chloride to synthesize TMA-chloride before the latter

---

* Corresponding author. Tel.: +886-2-25925252x2977; fax: +886-2-25861939.

E-mail address: cpyang@ttu.edu.tw (C.-P. Yang).

0014-3057/02/$ - see front matter
PII: S0014-3057(02)00076-9

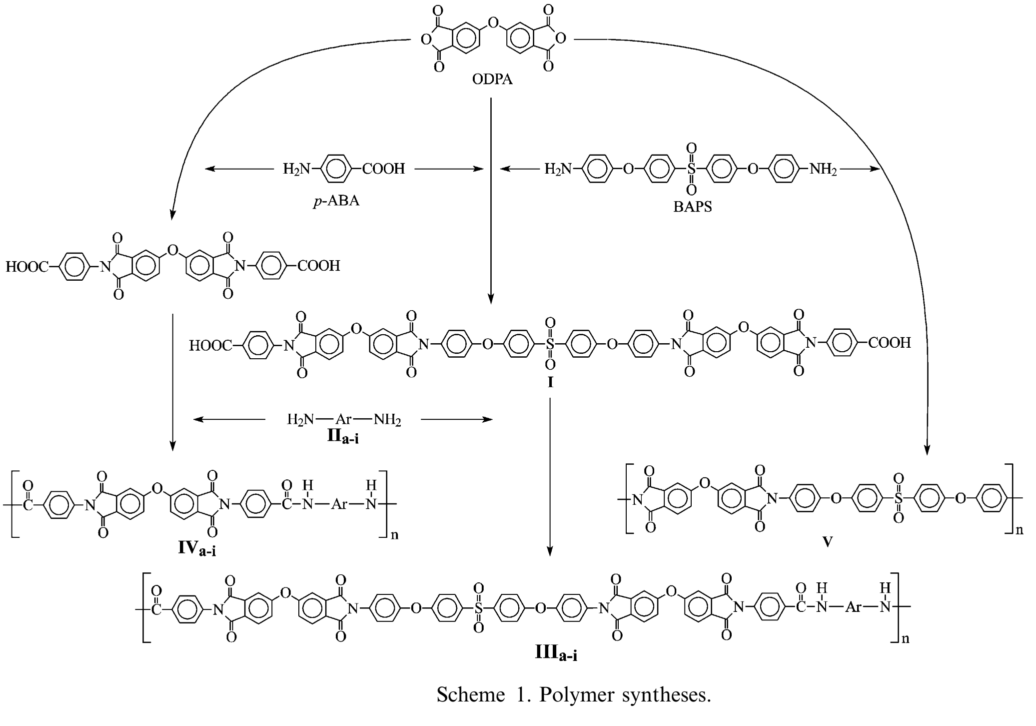
and diamine can produce poly(amide–imide) [17]. The second route goes through the imide-forming reaction, with amide-containing monomer serving as a medium; for example, amide-containing diamine is polycondensed with dianhydride to provide the poly(amide amic acid), which is then dehydrated to obtain poly(amide–imide) [18,19]. The last route goes through the amide-forming reaction from imide-containing monomers such as dicarboxylic acids or diamines. Imide-containing dicarboxylic acids usually come from the thermal imidization of diamines and TMA [20–26], from the condensation of dicarboxylic anhydride and amino acids [27–29], or from the dehydration of aromatic amino acids and TMA [30–32]. Then, these resultant imide-containing dicarboxylic acids react with aromatic diamines to synthesize aromatic poly(amide–imide)s by polycondensation.

In our laboratory, the dicarboxylic acid, *N*,*N*′-bis(4-carboxyphenyl)–4,4′-oxydiphthalimide, was prepared from the flexible ether group-containing 4,4′-oxydiphthalic anhydride (ODPA) and the rigid *p*-aminobenzoic acid (*p*-ABA). A series of poly(amide–imide)s (series **IV**, Scheme 1) was synthesized from the diacid and various aromatic diamines [33]. However, these polymers showed limited solubilities and poor film-forming ability. On the contrary, it was found that polyimide (**V**) synthesized from ODPA and BAPS had excellent solubility. In this study, BAPS, *p*-ABA, and ODPA were used to prepare a new-type tetraimide-dicarboxylic acid, which then reacted with various diamines to form poly(amide–imide–imide)s (**III**$_{a-i}$) by direct polycondensation. It was expected that synthesized polymers had significant improvement in solubilities and tensile properties. Various properties of the resultant poly(amide–imide–imide)s will be investigated and are compared with those of corresponding poly(amide–imide)s **IV**.

2. Experimental

2.1. Materials

4,4′-Oxydiphthalic anhydride (ODPA, Chriskev) was recrystallized from acetic anhydride before use. *p*-Aminobenzoic acid (*p*-ABA, TCI) and *m*-phenylenediamine (**II**$_a$, TCI) were vacuum-distilled before use. Other diamines including 4,4′-oxydianiline (**II**$_b$, TCI), 4,4′-thiodianiline (**II**$_c$, Chriskev), 4,4′-methylenedianiline (**II**$_d$, TCI), 1,4-bis(4-aminophenoxy)benzene (**II**$_e$, TCI), 1,3-bis(4-aminophenoxy)benzene (**II**$_f$, TCI), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**II**$_g$, Chriskev), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**II**$_h$, TCI), and 2,2-bis[4-(4-aminophenoxy)phenyl]sulfone (**II**$_i$, Chriskev) were used as received. *N*-methyl-2-pyrrolidone (NMP, Fluka) and pyridine (Py, Wako) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP, TCI) was used as received. Commercially available anhydrous calcium chloride



Scheme 1. Polymer syntheses.

($CaCl_2$) was dried under reduced pressure at 150 °C for 6 h prior to use.

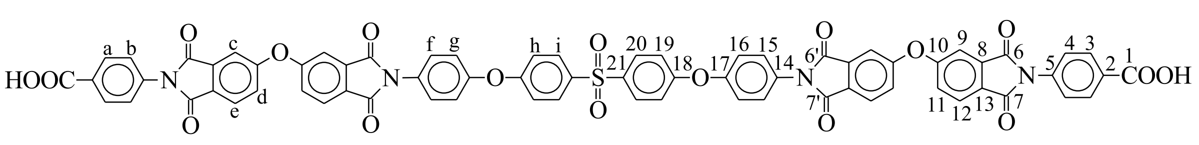
2.2. Synthesis of tetraimide-dicarboxylic acid (*I*)

A mixture of *p*-ABA (2.192 g; 16.00 mmol) and BAPS (3.456 g; 8.00 mmol) was first dissolved in NMP (48.00 ml). After the mixture was completely dissolved, ODPA (4.960 g; 16.00 mmol) was added to it in one portion. The mixture was stirred at room temperature for 2 h. Toluene (about 10 ml) was then added, and the mixture was heated at the reflux for about 3 h until water (about 0.70 ml) was distilled off azeotropically via a Dean-Stark trap. After complete removal of water, the residual toluene was then distilled off under reduced pressure. After cooling, the obtained solution was trickled into stirred water and the precipitated product was collected by filtration, washed several times with water, and dried in a vacuum to give diacid **I**; mp 325–327 °C (by Differential scanning calorimeter, DSC).

IR ν_{max} (KBr): 3500–2500 (acid –OH), 1778 (imide, symmetric C=O stretching), 1716 (acid C=O stretching and asymmetric imide C=O stretching), 1375 (imide, imide ring vibration, axial), 1107 (imide, imide ring vibration, transverse), and 744 cm^{-1} (imide, imide ring vibration, out of plane).

^1H NMR (400 MHz, DMSO-d_6):$\delta = 8.09, 7.98$ ($H_a + H_b + H_e$), 7.63, 7.53, ($H_c + H_d + H_f + H_i$), 7.31, 7.21 ($H_g + H_h$). ^{13}C NMR (100 MHz, DMSO-d_6):$\delta = 168.77$ (C^1), 168.26, 168.11, 167.94, 167.78 ($C^6 + C^{6'} + C^7 + C^{7'}$), 162.93 ($C^{10} + C^{18}$), 155.98 ($C^{17}$), 137.34, 137.16 ($C^5 + C^{21}$), 136.03 ($C^8$), 131.46 ($C^3 + C^{14}$), 130.86 ($C^{20}$), 129.97 ($C^{12}$), 128.47 ($C^2 + C^4$), 127.78 ($C^{13}$), 126.59 ($C^{11} + C^{15}$), 121.90 ($C^{19}$), 119.73 ($C^{16}$), 115.12 ($C^9$).

Analysis (wt.%) calculated for $C_{70}H_{38}N_4O_{18}S$: C, 66.99; H, 3.05; N, 4.46; found: C, 66.91; H, 3.07; N, 4.37.



2.3. Synthesis of poly(amide–imide–imide)s

A typical example of polycondensation is described as follows. A mixture of tetraimide-diacid **I** (1.255 g; 1.00 mmol), diamine $\mathbf{II}_g$ (0.410 g; 1.00 mmol), $CaCl_2$ (0.30 g), Py (0.90 ml), TPP (0.60 ml), and NMP (5.00 ml) was heated while being stirred at 100 °C for 3 h. The viscosity of reaction solutions increased after 1 h, and an additional NMP (3.00 ml) was added to the reaction mixture. At the end of the reaction, the obtained polymer solution was trickled into stirred methanol (400 ml). The stringy polymer was washed thoroughly with hot water and methanol, collected by filtration and dried at 100 °C under reduced pressure. The inherent viscosity of the polymer in DMAc at a 0.50 g/dl concentration at 30 °C was 0.99 dl/g. All other poly(amide–imide–imide)s were synthesized in a similar procedure.

2.4. Preparation of the poly(amide–imide–imide) films

A polymer solution of approximately 10% was made by the dissolving of poly(amide–imide–imide) in DMAc. The solution was poured into a glass culture dish 9 cm in diameter that was placed in a 90 °C oven overnight to remove the solvent. Then, the obtained semidried polymer film was stripped from the glass substrate and further dried in vacuum at 160 °C for 6 h. The obtained films were about 0.05 mm thick.

2.5. Measurements

^1H and ^{13}C NMR spectra were determined on a Jeol EX-400 FT-NMR spectrometer. Infrared spectra were recorded on a Horiba Fourier-transform infrared spectrometer FTIR-720. Elemental analyses were carried out with a Perkin–Elmer Model 2400 C, H, N analyzer. The inherent viscosities of all polymers were determined using a Cannon-Fenske viscometer. DSC traces were measured on TA Instruments DSC 2010 at the rate of 15 K/min in flowing nitrogen (40 cm^3/min). Thermogravimetric analysis (TGA) was conducted with a TA Instrument TGA 2050. Experiments were carried out on 10 ± 2 mg samples heated in flowing nitrogen (100 cm^3/min) at a heating rate of 20 K/min. An Instron Universal Tester Model 1130 with a load cell of 5 kg was used to study the stress–strain behavior of the sample. A gauge length of 2 cm and a strain rate of 5 cm/min were adopted for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6.0 cm long, and about 0.05 mm thick), and an average of at least five individual determinations was reported.

3. Results and discussion

3.1. Tetraimide-dicarboxylic acid synthesis

Tetraimide-dicarboxylic acid (**I**) was synthesized starting from the ring-opening addition of BAPS, ODPA, and *p*-ABA in a 1:2:2 molar ratio at room temperature in amide-type solvent (such as NMP or DMAc), followed by intramolecular cyclodehydration of the intermediate tetramic acid **I**′ (Scheme 2). The addition of *p*-ABA, ODPA, and BAPS may not form the structure of tetramic acid **I**′ completely in the initial period, and some other diacids (Scheme 3) were produced. However, the exchange reaction of amic acid was carried out during a long time of stir [34], and the product with the lowest free energy was prepared. From the molar ratio of monomers, **I**′ is a more stable structure among intermediates. Therefore, a higher purity of tetraimide-diacid **I** might be obtained after the cyclodehydration of **I**′. The structures of diacid **I** were confirmed by elemental analysis and IR, ^{1}H NMR, and ^{13}C NMR spectroscopy.

The FTIR characteristic absorptions of diacid **I** are shown in Fig. 1. As the diacid was prepared, the characteristic absorption bands of the imide ring were observed at 1778, 1716, 1375, 1107, and 744 cm^{-1}, and those of the anhydride and carboxyl groups of monomers at 1851 (acid C=O) and 1269 (C–O–C) cm^{-1} disappeared. The diacid **I** is also confirmed by NMR spectra (Fig. 2). In the ^{1}H NMR spectrum, the protons $H_{a,b,e}$ adjacent to the carbonyl acid or imide ring (ortho-oriented protons) resonated at the farthest downfield region, due to the inductive effect of the carboxyl group and the resonance of the imide ring; the H_i adjacent to sulfonyl group and $H_{c,d}$ ortho-oriented to aromatic ether shifted to the upfield region, due to the inductive effect of the sulfonyl group and the shielding effect of the ether unit. The $H_{g,h}$ appeared at higher filed than the rest protons in that it was less affected by other groups. To calculate purity of **I**, it was assumed that the structures of m = 0 and 1 were the main components (Scheme 3), so that the proportion of m = 1 could be *x* and that of m = 0 could be *y*. From the integral ratios of protons $H_{a,b,e}$ and $H_{c,d,f,i}$ in Fig. 2

$$\begin{cases} \dfrac{\mathrm{H}_{a,b,e}}{\mathrm{H}_{c,d,f,i}} = \dfrac{12x + 10y}{16x + 4y} \fallingdotseq \dfrac{1.0000}{1.2959} \\ x + y = 1 \end{cases}$$

It was noticed that *x* was more than 95%; therefore, almost all the formed diacid had a structure of **I**. The ^{13}C NMR spectrum of **I** shows 19 signals, including 5 signals of carbonyl of the imide ring and 14 signals of carbon of benzene. C^1 appeared at 168.77 ppm and $C^{6,6',7,7'}$ displayed four signals (168.26, 168.11, 167.94, 167.78 ppm). It will give off 18 signals for carbon of benzene, but the actual measurement showed 14 signals due to overlap of some carbons.

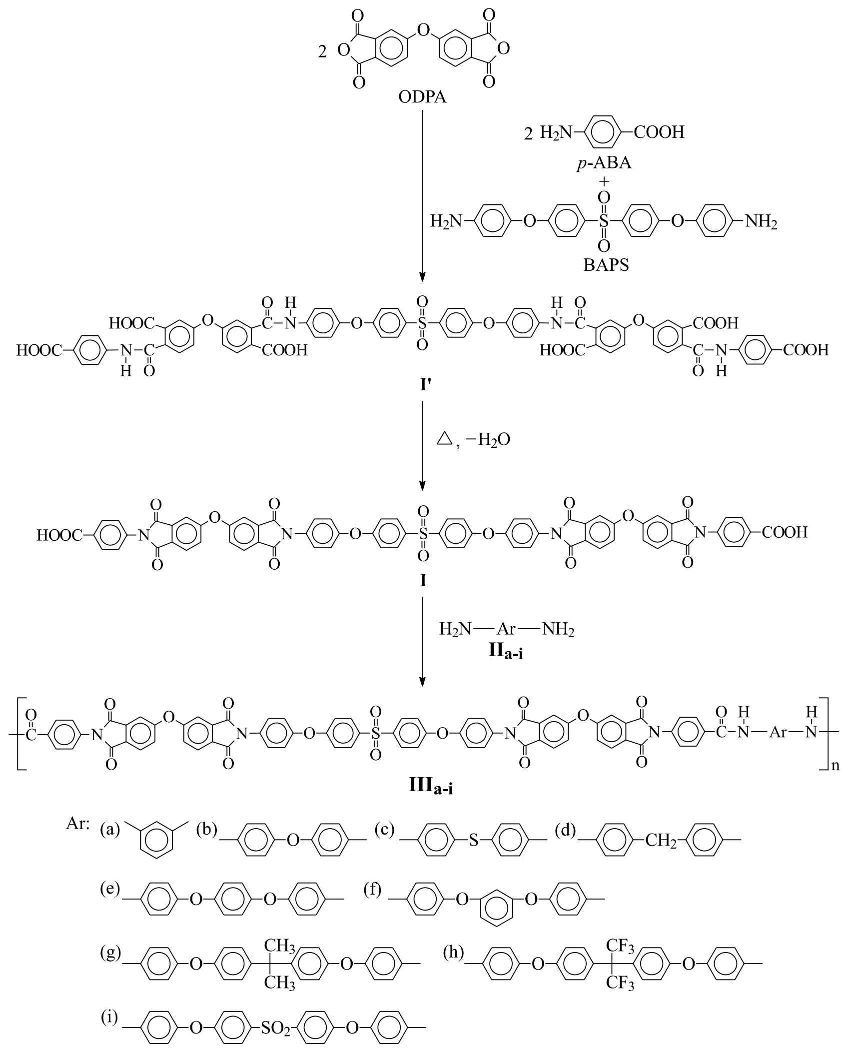
3.2. Polymer synthesis

A series of poly(amide–imide–imide)s $\mathbf{III}_{a\text{–}i}$ was synthesized from **I** and various diamines by means of direct polycondensation with TPP/Py as the condensing agent in NMP in the presence of calcium chloride. Polymerization can also proceed directly using the resultant solution of diacid synthesis. The results of the preparation of poly(amide–imide–imide)s are summarized in Table 1. All the reactions went on smoothly in homogeneous solutions under conditions listed in Table 1. In some cases, higher molecular weights of these polymers could be obtained by using a higher initial reactant concentration and adding a proper amount of supplemental NMP into the viscous reaction medium before the formation of swollen gel (physical entanglements). Besides, an advantage of poly(amide–imide–imide) synthesis from large molecular weight **I** is that a large product can be obtained by using a small amount of TPP. In other words, when the same amount of TPP is used, the same mole of a polymer in this study and in other reports is formed, but the weight of the polymer in this study is larger. Therefore, new-type poly(amide–imide–imide)s could significantly reduce the synthetic cost and were thus helpful in industrializing direct polycondensation.

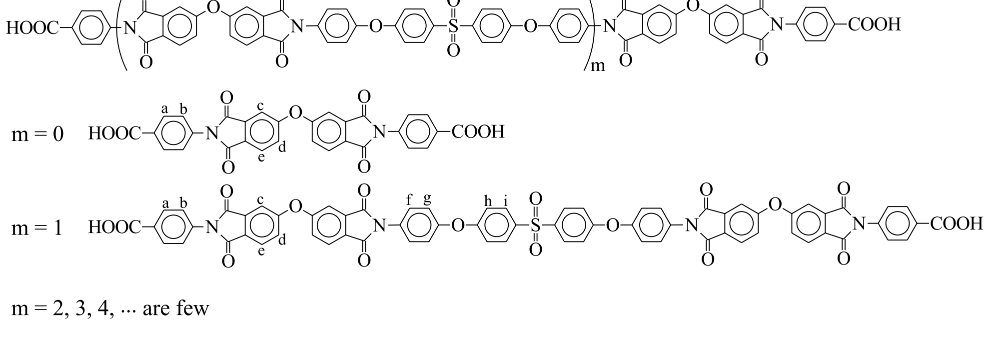
The inherent viscosities of the **III** series polymers were 0.71–0.99 dl/g. Most of the poly(amide–imide–imide)s could be solution cast into transparent and tough films, indicating a high molecular weight. The composition and structures of these poly(amide–imide–imide)s were characterized by their IR spectra and elemental analyses. A typical IR spectrum is shown in Fig. 1. The FTIR spectrum of polymer $\mathbf{III}_h$ exhibited characteristic absorption bands for the imide ring at 1778, 1724 (asymmetrical and symmetrical C=O stretching vibration), 1373 (C–N stretching vibration), 1107, and 744 cm^{-1} (imide ring deformation). The absorptions of amide groups appeared at 3373 (N–H stretch) and 1676 cm^{-1} (C=O stretch).

3.3. Polymer properties

The qualitative solubility of poly(amide–imide–imide)s in various solvents is listed in Table 1. All polymers had excellent solubilities in NMP, DMAc, DMF, DMSO, and *m*-cresol. The solubilities of series **III** polymers in pyridine varied with the structures of diamines used in the synthesis. $\mathbf{III}_{a\text{–}f}$ with Ar structures of short linkage or triphenylene–diether were partially soluble or insoluble in pyridine, but $\mathbf{III}_{g\text{–}i}$ with Ar structures of the flexible group (such as isopropylidene, hexafluoroisopropylidene, and sulfone) showed the best solubilities among these polymers. Compared with $\mathbf{IV}_{a\text{–}i}$, the **III**



Scheme 2. Preparation of poly(amide–imide–imide)s.



Scheme 3. Chemical structures of the tetraimide-dicarboxylic acid **I**.

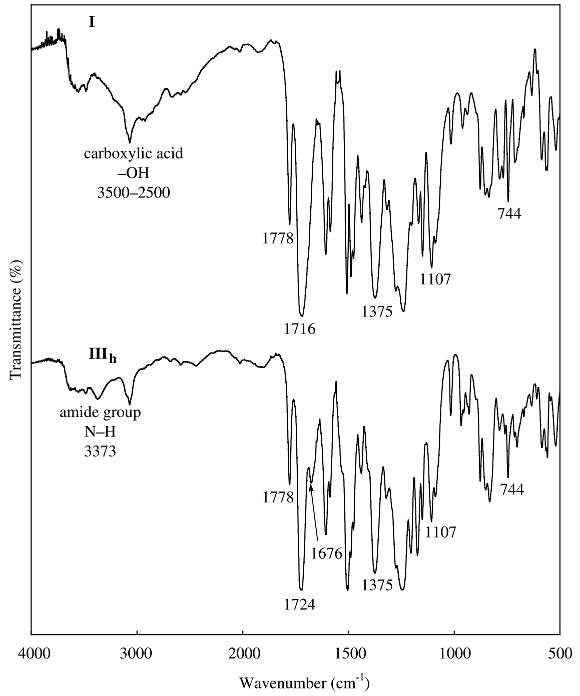


Fig. 1. FTIR spectra of tetraimide-diacid **I** and poly(amide–imide–imide) **III**$_h$.

series polymers clearly exhibited a better solubility. This might be due to the presence of the flexible linkage in the diacid **I**, which disturbed the co-planarity of aromatic units to reduce the packing efficiency and the crystallinity.

With the exception of the brittle behavior of polymer **III**$_{b,e}$, all the poly(amide–imide–imide)s were cast into transparent, flexible, and tough films from polymer solutions of DMAc. The tensile properties of the polymer films were determined by an Instron machine. The results are summarized in Table 2. These films had tensile strengths at break of 94–100 MPa, elongations at break of 7–9%, and initial tensile moduli of 2.0–2.3 GPa. Two poly(amide–imide–imide)s in this series necked under tension and exhibited moderate elongation to break, indicating a ductile nature. This series of poly(amide–imide–imide)s all possessed good tensile properties, suggesting that these poly(amide–imide–imide)s can be applied as new materials for engineering plastics. On comparing tensile properties of polymers **III** with their analogous **IV**, series **III** polymers showed good film-forming ability. Except for **IV**$_a$, the other polymers **IV**$_{b–i}$ couldn't be cast into films or formed brittle films, due to poor solubility and high level of crystallinity [33].

The thermal properties of all the poly(amide–imide–imide)s were evaluated by thermogravimetry (TG) and

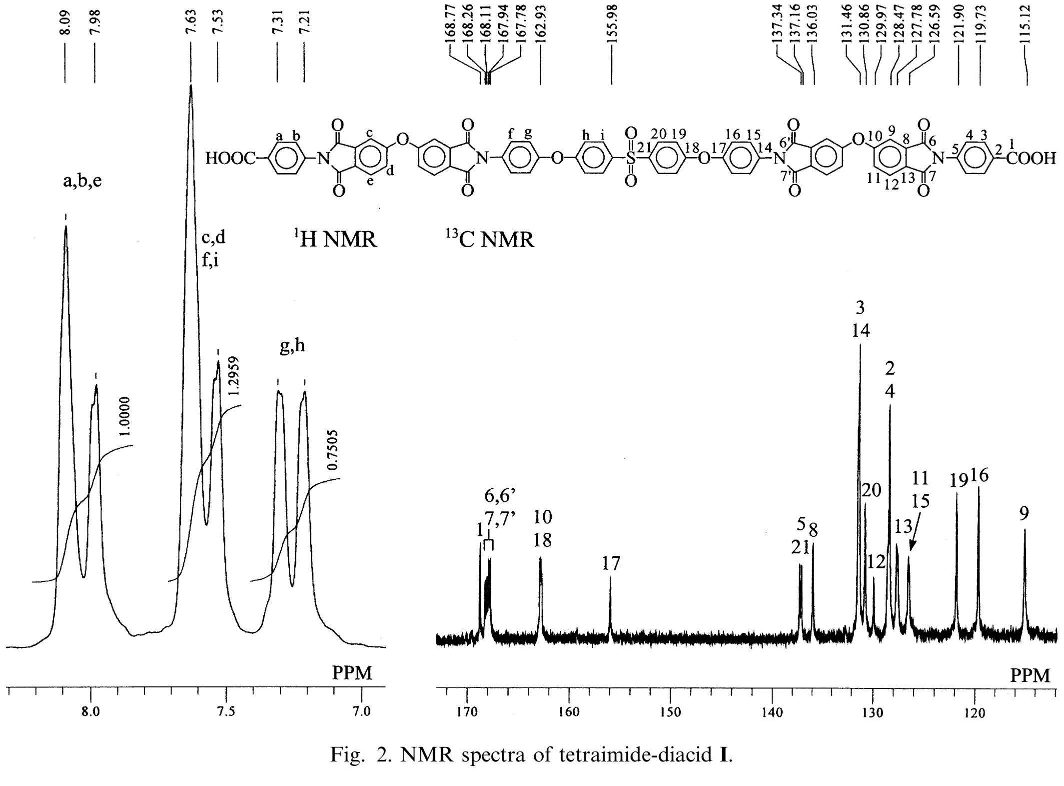


Fig. 2. NMR spectra of tetraimide-diacid **I**.

Table 1
Synthesis[a] and solubility[b] of poly(amide–imide–imide)s

Polymer	Additional amount of NMP (ml)	η_{inh} (dl/g)[c]	Solvent[d]					
			NMP	DMAc	DMF	DMSO	*m*-Cresol	Py
III$_a$	3	0.75	++	++	++	++	++	±
III$_b$	–	0.78	++	++	++	++	++	±
III$_c$	1	0.81	++	++	++	++	++	±
III$_d$	3	0.71	++	++	++	++	++	–
III$_e$	4	0.82	++	++	++	++	++	–
III$_f$	1	0.86	++	++	++	++	++	–
III$_g$	3	0.99	++	++	++	++	++	++
III$_h$	–	0.79	++	++	++	++	++	++
III$_i$	–	0.76	++	++	++	++	++	++
IV$_a$			++	++	++	++	++	S
IV$_b$			S	S	–	S	–	S
IV$_c$			S	S	–	S	–	–
IV$_d$			–	–	–	–	–	–
IV$_e$			–	–	–	–	–	–
IV$_f$			–	–	–	–	–	–
IV$_g$			++	S	S	S	S	S
IV$_h$			++	+	++	++	++	++
IV$_i$			++	S	S	S	S	S

(++) soluble at room temperature, (+) soluble after heating, (±) partially soluble, (S) swelling, (–) insoluble.

[a] Polymerization was carried out with 1 mmol of each monomer in 5 ml of NMP, 0.3 g of $CaCl_2$, 0.9 ml of Py and 0.6 ml of TPP at 100 °C for 3 h.

[b] Solubility: measured at a polymer concentration of 0.05 g/ml in 24 h.

[c] Measured at a polymer concentration of 0.5 g/dl in DMAc at 30 °C.

[d] NMP: *N*-methyl-2-pyrrolidone; DMAc: *N*,*N*-dimethylacetamide; DMF: *N*,*N*-dimethylformamide; DMSO: dimethyl sulfoxide; Py: pyridine.

Differential scanning calorimetry (DSC). The thermal behavior data of all polymers are listed in Table 3. DSC measurements were conducted at a heating rate of 15 K/min in nitrogen. Quenching from the elevated temperatures (≈400 °C) to room temperature in air gave predominantly amorphous samples so that the glass transition temperatures (T_g) of all poly(amide–imide–imide)s could be easily measured in the second heating traces of DSC. The T_g values of the poly(amide–imide–imide)s **III** were in the range of 265–291 °C, depending on the structure of the diamine component and following with the increasing stiffness of the polymer backbones. Insertion of the flexible ether group increased the overall flexibility of the polymer chain and, as a result, resulted generally in a decrease in T_g as evidenced by T_g order shown in Table 3: **III**$_a$ > **III**$_{b,c,d}$ > **III**$_{e,f}$. **III**$_{g,h}$, based on **II**$_{g,h}$ with a bulky pendent group, increased steric hindrances, thus causing its macromolecular chains to rotate at higher temperature without lowering T_g. **III**$_i$ with the polar sulfone groups in polymer backbones possessed higher T_g value than corresponding **III**$_{g,h}$. For isomers, **III**$_e$, whose diamine structures were all *para*-oriented, showed higher T_g values than did **III**$_f$, derived from *meta*-oriented diamines. When comparing **III**$_{a–i}$ with **IV**$_{a–i}$, the **III** series displayed higher T_g values than the corresponding **IV**. This was attributed to the higher proportion of the imide and polar sulfonyl groups in the **III** series polymer backbones.

Table 2
Tensile properties of poly(amide–imide–imide) films[a]

Polymer	Tensile strength at yield (MPa)	Tensile strength at break (MPa)	Elongation at break (%)	Initial tensile modulus (GPa)
III$_a$	–	100	9	2.2
III$_c$	97	96	9	2.2
III$_d$	94	94	9	2.3
III$_f$	–	95	7	2.2
III$_g$	–	96	8	2.0
III$_h$	–	98	9	2.0
III$_i$	–	98	7	2.3
IV$_a$	–	101	9	2.5

[a] Films were cast from slow evaporation of polymer solutions in DMAc.

The thermostabilities of the poly(amide–imide–imide)s were examined by TGA measurements. The temperatures at 10% weight loss (T_{10}) in nitrogen atmosphere

Table 3
Thermal properties of poly(amide–imide–imide)s

Polymer	DSC	TGA	
	T_g (°C)[a]	T_{10} (°C)[b]	Char yield (%)[c]
$\mathbf{III}_a$	291	562	51
$\mathbf{III}_b$	286	561	52
$\mathbf{III}_c$	287	567	60
$\mathbf{III}_d$	289	554	52
$\mathbf{III}_e$	278	565	55
$\mathbf{III}_f$	265	572	56
$\mathbf{III}_g$	272	547	51
$\mathbf{III}_h$	273	569	57
$\mathbf{III}_I$	283	572	54
$\mathbf{IV}_a$	249	514	56
$\mathbf{IV}_b$	238	532	58
$\mathbf{IV}_c$	248	528	60
$\mathbf{IV}_d$	243	522	50
$\mathbf{IV}_e$	–	533	51
$\mathbf{IV}_f$	245	520	66
$\mathbf{IV}_g$	246	539	60
$\mathbf{IV}_h$	243	548	57
$\mathbf{IV}_i$	246	556	52

[a] Midpoint of baseline shift in the second heating DSC trace with a heating rate of 15 K/min under a nitrogen atmosphere.

[b] Temperatures at which 10% weight loss were recorded by TGA at a heating rate of 20 K/min under a nitrogen atmosphere.

[c] Residual weight % at 800 °C under a nitrogen atmosphere.

were determined from the original thermograms and are tabulated in Table 3. T_{10} values of polymers **III** were in the range of 547–572 °C. $\mathbf{III}_{d,g}$ exhibited lower T_{10} values than the others because the aliphatic groups (CH_2 or CH_3) of diamine segments were decomposed easily in the heating process. The fluorine-containing poly(amide–imide–imide) $\mathbf{III}_h$ had a better thermal stability than its nonfluoro analogous $\mathbf{III}_g$ did because the C–F bond of the CF_3 group is stronger than that of the CH_3 group. The thermogravimetric traces indicate that polymers **III** possess high thermal stability with no significant weight loss up to approximately 500 °C. The char yields of all polymers at 800 °C were above 51%. When compared with polymers **IV**, all of series **III** had higher T_{10} values as a result of a higher proportion of the thermostable imide group in the main chain.

4. Conclusions

A series of new-type poly(amide–imide–imide)s $\mathbf{III}_{a\text{–}i}$ with moderate to high molecular weights was successfully synthesized. These polymers showed excellent solubilities and could be made into transparent and tough films upon casting from DMAc solution, reflecting good film-forming ability. Their polymer films were flexible and tough, and some of them exhibited yield points. Besides, these polymers were characterized by excellent thermal stability as well as high glass transition temperatures, demonstrating a good combination of properties and processability.

Acknowledgements

The authors are grateful to the National Science Council of the Republic of China for the support of this work (Grant NSC 90-2216-E-036-016).

References

[1] Cassidy PE. Thermally stable polymers. New York: Dekker; 1980.
[2] Yang HH. Aromatic high-strength fibers. New York: Wiley; 1986.
[3] Seymour RB, Carraher CE. Polymer chemistry: an introduction. New York: Dekker; 1981.
[4] Yang CP, Chen WT. Makromol Chem 1992;193:2323.
[5] Yang CP, Lin JH. J Polym Sci, Part A: Polym Chem 1996;34:341.
[6] Bell VL, Stump BL, Gager H. J Polym Sci, Part A: Polym Chem 1976;14:2275.
[7] Takekoshi T, Wirth JG, Heath DR, Kochanocoski JE, Manello JS, Webber MT. J Polym Sci, Part A: Polym Chem 1980;18:3069.
[8] Feld WA, Ramalingam B, Harris FW. J Polym Sci, Part A: Polym Chem 1983;21:319.
[9] Ghatge ND, Shinde BM, Mulik UP. J Polym Sci, Part A: Polym Chem 1984;22:3359.
[10] Imai Y, Malder NN, Kakimoto M. J Polym Sci, Part A: Polym Chem 1984;22:2189.
[11] Jeong HJ, Oishi Y, Kakimoto M, Imai Y. J Polym Sci, Part A: Polym Chem 1991;29:39.
[12] Oishi Y, Ishida M, Kakimoto M, Imai Y, Kurosaki T. J Polym Sci, Part A: Polym Chem 1992;30:1027.
[13] Frey HE. Standard Oil Co. US Patent 3 300 420, 1967.
[14] Hitachi Chem. Co. France Patent 1 473 600, 1967.
[15] Sambeth J. Soc Rhodiaceta. France Patent 1 498 015, 1967.
[16] Kakimoto M, Akiyama R, Negi YS, Imai Y. J Polym Sci, Part A: Polym Chem 1988;26:99.
[17] Imai Y, Maldar NN, Kakimoto M. J Polym Sci, Part A: Polym Chem 1985;23:2077.
[18] Dezern JF. J Polym Sci, Part A: Polym Chem 1988;26:2157.
[19] Bower GM, Frost LW. J Polym Sci, Part A-1 1963;3135.
[20] Yang CP, Chen RS, Chang CC. Colloid Polym Sci 2000;278:1043.
[21] Yang CP, Chen RS, Chen JA. J Polym Sci, Part A: Polym Chem 2000;38:1.
[22] Yang CP, Wei CS. Polymer 2001;42:1837.
[23] Ghosh M. Angew Makromol Chem 1989;172:165.
[24] de la Campa JG, de Abajo J. Eur Polym J 1983;19:667.
[25] Wrasidlo W, Augl JM. J Polym Sci, Part A-1 1969;7:321.

[26] Venkatesan D, Srinivasan M. Polym Int 1992;29:275.
[27] Yang CP. J Polym Sci, Part A: Polym Chem 1979;17:3255.
[28] Yang CP, Hsiao SH, Lin JH. J Polym Sci, Part A: Polym Chem 1992;30:1865.
[29] Yang CP, Chen RS, Hung KS. Polymer 2001;42:4569.
[30] Maiti S, Ray A. J Appl Polym Sci 1983;28:225.
[31] Maiti S, Ray A. J Polym Sci, Part A: Polym Chem 1983;21:999.
[32] Hsiao SH, Yang CP. J Polym Sci, Part A: Polym Chem 1990;28:1149.
[33] Yang CP, Chen RS, Hung KS, Woo EM. Polym Int, in press.
[34] Yang CP, Hsiao SH. J Appl Polym Sci 1985;30:2883.