

New poly(amide-imide) syntheses, 4^{a)}

Poly(amide-imide)s derived from 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene and various bis(trimellitimide)s

Chin-Ping Yang*, Sheng-Huei Hsiao, Jiun-Hung Lin

Department of Chemical Engineering, Tatung Institute of Technology,
40 Chungshan North Rd. 3rd Sec., Taipei, Taiwan, Republic of China

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SUMMARY:

Fifteen bis(trimellitimide)s **2a–o** were prepared by condensation of the corresponding aliphatic or aromatic diamines with trimellitic anhydride. A series of structurally new poly(amide-imide)s were synthesized by the direct polycondensation of these bis(trimellitimide)s with 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene using triphenyl phosphite and pyridine as condensing agents in *N*-methyl-2-pyrrolidone (NMP). The resultant poly(amide-imide)s have inherent viscosities in the range between 0,72 and 2,73 dL/g at 30 °C in *N,N*-dimethylacetamide (cf. Tab. 2). The polymers are amorphous and readily soluble in polar aprotic solvents such as *N,N*-dimethylacetamide (DMAc) and NMP. Transparent and tough films can be cast from their solutions. Most aliphatic-aromatic poly(amide-imide)s show a glass transition in the range between 203 and 242 °C in their differential scanning calorimetry (DSC) traces, whereas the wholly aromatic poly(amide-imide)s show no discernible transition before decomposition. The thermal stability of the polymers was evaluated by thermogravimetry which showed the 10% weight-loss temperatures in the range between 414 and 459 °C in air and between 451 and 578 °C in a nitrogen atmosphere for the aliphatic-aromatic poly(amide-imide)s and above 500 °C in both air and nitrogen atmosphere for the wholly aromatic poly(amide-imide)s.

Introduction

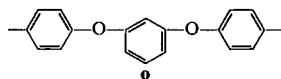
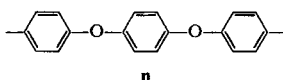
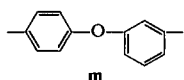
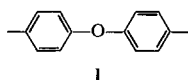
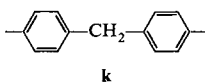
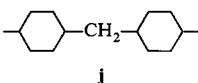
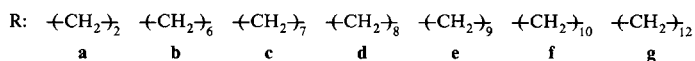
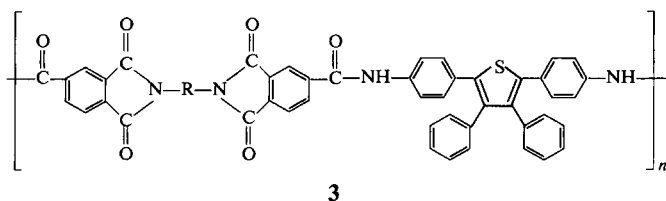
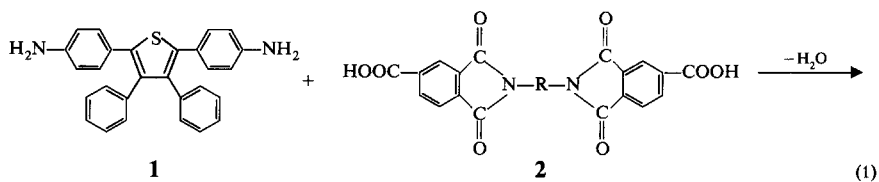
Aromatic polyimides belong to the most important, thermally stable polymers. However, their application was limited due to their infusibility and insolubility which make them difficult to process. To overcome this drawback various copolyimides have been developed. For example, a poly(amide-imide) was developed as one of alternative materials offering a compromise between excellent thermal stability and processability.

Direct polycondensation promoted by organic aryl phosphites and organic bases such as pyridine is a highly useful laboratory method for the synthesis of polyamides¹⁾; aliphatic-aromatic and wholly aromatic polyamides were readily obtained from combinations of aromatic diamines with aliphatic and aromatic dicarboxylic acids, respectively. At present, the phosphorylation reaction is still a very popular means for screening new polyamides^{2–4)}, because relatively small amounts of simple monomers are required for the synthesis. According to earlier papers^{5–10)} we have successfully applied this direct polycondensation technique to the synthesis of

^{a)} Part 3: cf. ¹³⁾.

poly(amide-imide)s from imide-containing dicarboxylic acids and aromatic diamines. In the most recent papers¹¹⁻¹³, this technique was applied effectively for screening novel poly(amide-imide)s.

In recent years, Imai et al.¹⁴ have developed soluble high-temperature polymers which possess a highly phenylated tetraphenylthiophene moiety as the key structure. In the first¹¹ and second¹² of this series of papers the tetraphenylthiophene containing poly(amide-imide)s were prepared from combinations of 2,5-bis(4-trimellitimidophenyl)-3,4-diphenylthiophene with aromatic diamines or from combinations of 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene (**1**) with mono-trimellitimide- or pyromellitimide-containing dicarboxylic acids. The present work reports the preparation and characterization of another series of new poly(amide-imide)s with a tetraphenylthiophene moiety in the repeating unit of the polymer backbone by using various bis(trimellitimide)s and the tetraphenylthiophenediamine **1** as monomers.



Experimental part

Materials

Trimellitic anhydride (Wako) was used without previous purification, *p*-Phenylenediamine and *m*-phenylenediamine were vacuum-distilled before use. All other diamines were of high purity when received from the manufacturers and used without any further purification. Commercially obtained anhydrous calcium chloride was dried under vacuum at 180 °C for 10 h. *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP) was purified by distillation under reduced pressure. The bis(trimellitide)s were obtained by a similar procedure, as reported previously⁷⁾, from the condensation of an α,ω -diaminoalkane or an aromatic diamine with trimellitic anhydride in a mole ratio 1 : 2. According to the reported method¹⁵⁾, 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene (1) was synthesized starting from tetraphenylthiophene, which was easily prepared by the reaction of benzyl chloride with powdered sulfur at elevated temperature.

Polycondensation

A typical example of a polycondensation was conducted as follows. A mixture of 0,738 g (1,25 mmol) of diacid **2n**, 0,522 g (1,25 mmol) of 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene (1), 0,8 g of calcium chloride, 0,8 mL (2,5 mmol) of triphenyl phosphite, 1,5 mL of pyridine, and 8 mL of NMP were heated with stirring at 100 °C for 3 h under nitrogen. The obtained polymer solution was trickled on 500 mL of methanol giving rise to a stringy precipitate which was washed thoroughly with methanol and hot water, collected by filtration, and dried. The yield was quantitative. The inherent viscosity of a 0,5 g/dL polymer solution in *N,N*-dimethylacetamide (DMAC) 5 wt.-% LiCl was 2,01 dL(g at 30 °C. IR (film) in cm^{-1} : 1780 and 1725 (C=O imide), 1110 and 725 (imide ring), 1670 (C=O amide), 3340 (N—H amide).

| | | | | |
|--|-------|---------|--------|--------|
| $(\text{C}_{58}\text{H}_{34}\text{N}_4\text{O}_7\text{S} \cdot 2\text{H}_2\text{O})_n$ | Calc. | C 72,04 | H 3,96 | N 5,79 |
| | Found | C 72,43 | H 3,26 | N 5,55 |

All other poly(amide-imide)s were synthesized by an analogous procedure. The elemental analysis values of the polymers are in good agreement with the calculated values, assuming that the poly(amide-imide)s absorbed one or two molecules of H₂O per repeating unit. It is well-known that polyamides show strong tendency of absorbing moisture due to the hydrophilic nature of the amide groups.

Measurements

Elemental analyses were conducted in a Perkin-Elmer Model 240 C,H,N-analyzer.

IR spectra were recorded on a Jasco FT/IR-7000 Fourier-transform infrared spectrometer.

The inherent viscosities were measured with a Cannon-Fenske viscosimeter in a thermostat bath at 30 °C.

The differential scanning calorimeter (DSC) traces were measured on a DuPont 910 differential scanning calorimeter coupled to a DuPont 1090 thermal analyzer at the rate of 20 °C/min in flowing nitrogen (30 cm^3/min).

Thermogravimetry (TG) was conducted with a DuPont 951 thermogravimetric analyzer coupled to a DuPont 1090 thermal analyzer. The experiments were carried out on 10 ± 2 mg samples heated in flowing nitrogen (50 cm^3/min) at a heating rate of 20 °C/min.

The wide-angle X-ray measurements were performed at room temperature (about 25 °C) with film specimens about 0,1 mm thick on a Rigaku Geiger Flex D-Max III_a X-ray diffractometer, using Ni-filtered CuK_α radiation (40 kV, 15 mA). The scanning rate was 2 °/min.

An Instron Universal Tester Model 1130 with a load cell 5 kg was used to study the stress-strain behavior of the samples. A gauge of 2 cm and a strain rate of 5 cm/min were used for this study.

The measurements were performed at room temperature with film specimens (0,5 cm wide, 6 cm long, and about 0,1 mm thick) and an average of at least five individual determinations was used.

Results and discussion

Polymer synthesis

A class of bis(trimellitimide)s **2a–o** containing preformer imide rings were readily obtained by the condensation of trimellitic anhydride with the corresponding aliphatic or aromatic diamines. They were prepared via the two-stage procedure that included ring-opening addition of the diamine with two equivalent amounts of trimellitic

Tab. 1. Yields and properties of the diimide-diacids **2a–o**

| Compound | Yield in % | M.p. ^{a)} in °C | Formula (molecular weight) | Elemental analyses | | | |
|-----------|------------|----------------------------|--|--------------------|-------|------|------|
| | | | | Calc. | %C | %H | %N |
| 2a | 85 | 364 (362) ^{b)} | C ₂₀ H ₁₂ N ₂ O ₈ (408,32) | Calc. | 58,83 | 2,96 | 6,86 |
| | | | | Found | 58,70 | 2,90 | 6,73 |
| 2b | 80 | 321 (321) ^{b)} | C ₂₄ H ₂₀ N ₂ O ₈ (464,42) | Calc. | 62,07 | 4,34 | 6,03 |
| | | | | Found | 61,95 | 4,03 | 5,96 |
| 2c | 91 | 228 (222) ^{c)} | C ₂₅ H ₂₂ N ₂ O ₈ (478,46) | Calc. | 62,76 | 4,63 | 5,85 |
| | | | | Found | 62,50 | 4,51 | 5,13 |
| 2d | 90 | 243 (243) ^{c)} | C ₂₆ H ₂₄ N ₂ O ₈ (491,99) | Calc. | 63,47 | 4,92 | 5,69 |
| | | | | Found | 63,29 | 4,55 | 5,56 |
| 2e | 90 | 208 (205) ^{c)} | C ₂₇ H ₂₆ N ₂ O ₈ (506,11) | Calc. | 64,08 | 5,18 | 5,52 |
| | | | | Found | 63,91 | 4,78 | 5,42 |
| 2f | 92 | 226 (224) ^{c)} | C ₂₈ H ₂₈ N ₂ O ₈ (520,24) | Calc. | 64,64 | 5,42 | 5,38 |
| | | | | Found | 64,46 | 5,17 | 5,25 |
| 2g | 90 | 210 (210) ^{c)} | C ₃₀ H ₃₂ N ₂ O ₈ (548,49) | Calc. | 65,69 | 5,88 | 5,11 |
| | | | | Found | 65,56 | 5,70 | 5,09 |
| 2h | 99 | 465 | C ₂₄ H ₁₂ N ₂ O ₈ (456,37) | Calc. | 63,16 | 2,65 | 6,14 |
| | | | | Found | 63,07 | 2,67 | 6,02 |
| 2i | 98 | 409 (456,37) | C ₂₄ H ₁₂ N ₂ O ₈ (456,37) | Calc. | 63,16 | 2,65 | 6,14 |
| | | | | Found | 63,02 | 2,70 | 6,10 |
| 2j | 93 | 306 (554,54) | C ₃₁ H ₂₆ N ₂ O ₈ (554,54) | Calc. | 67,14 | 4,72 | 5,05 |
| | | | | Found | 67,06 | 4,58 | 5,09 |
| 2k | 98 | 360 (362) ^{b)} | C ₃₁ H ₁₈ N ₂ O ₈ (546,47) | Calc. | 68,13 | 3,32 | 5,12 |
| | | | | Found | 68,14 | 3,27 | 5,22 |
| 2l | 95 | 378 (374) ^{d)} | C ₃₀ H ₁₆ N ₂ O ₉ (548,46) | Calc. | 65,69 | 2,94 | 5,10 |
| | | | | Found | 65,52 | 2,98 | 5,35 |
| 2m | 92 | 353 (548,46) | C ₃₀ H ₁₆ N ₂ O ₉ (548,46) | Calc. | 65,69 | 2,94 | 5,10 |
| | | | | Found | 65,55 | 2,97 | 5,20 |
| 2n | 99 | 399 (640,56) | C ₃₆ H ₂₀ N ₂ O ₁₀ (640,56) | Calc. | 67,50 | 3,15 | 4,37 |
| | | | | Found | 67,46 | 3,19 | 4,32 |
| 2o | 99 | 350 (640,56) | C ₃₆ H ₂₀ N ₂ O ₁₀ (640,56) | Calc. | 67,50 | 3,15 | 4,37 |
| | | | | Found | 67,48 | 3,18 | 4,34 |

a) Melting points above 300 °C were determined by using differential scanning calorimetry.

b) See ref. 16).

c) See ref. 17).

d) See ref. 18).

anhydride, followed by cyclodehydration to the imidodicarboxylic acids by means of toluene-water azeotropic distillation. Characterization data of all diimido-diacids used in this work are summarized in Tab. 1. 2,5-Bis(4-aminophenyl)-3,4-diphenylthiophene (**1**), prepared from benzyl chloride and sulfur according to the reported method¹⁵, was used here as the polymer-forming diamine for the preparation of poly(amide-imide)s.

A series of novel poly(amide-imide)s **3a–o** containing a tetraphenylthiophene moiety were synthesized from diamine **1** and various imide rings-containing dicarboxylic acids **2a–o** by the recently popular method using triphenyl phosphite as promoter in NMP in the presence of pyridine and calcium chloride¹¹ (Eq. (1)). The results of the preparation of poly(amide-imide)s are summarized in Tab. 2. These polymers were obtained in almost quantitative yields with inherent viscosities of 0,7–2,73 dL/g. The molecular weights of these polymers are sufficiently high to permit casting tough films.

Tab. 2 also lists the elemental analysis values of these poly(amide-imide)s. The elemental analysis values of the polymers were in good agreement with the calculated values, assuming that the poly(amide-imide)s absorbed one or two molecules of H₂O per repeating unit. Fig. 1 shows the representative Fourier-transform IR (FTIR) spectra of polymers **3f** and **3n**. The IR spectra showed characteristic absorptions for the imide ring at 1780 and 1725 cm⁻¹, characteristic for the asymmetrical and symmetrical carbonyl stretching vibration, and at 1100 and 725 cm⁻¹, due to ring deformation. Bands of amide groups appear at 3340, 1670, and 1595 cm⁻¹.

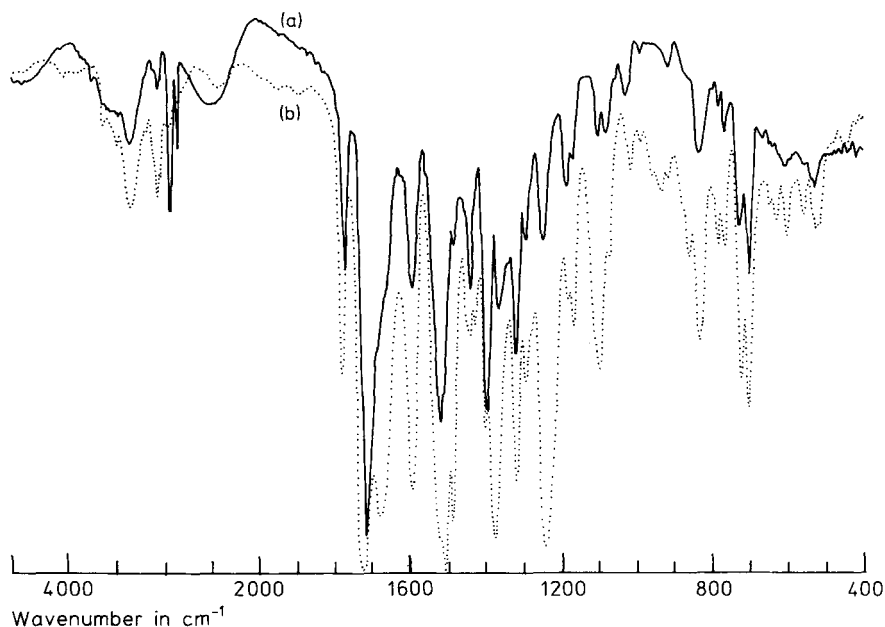


Fig. 1. Fourier-transform IR (film) spectra of poly(amide-imide)s **3f** (a) and **3m** (b)

Tab. 2. Inherent viscosities η_{inh} and elemental analyses of poly(amide-imide)s **3a–o**^{a)}

| Polymer | η_{inh} ^{b)} dL/g | Formula (molecular weight) | Elemental analyses | | | |
|-----------|------------------------------------|--|--------------------|-------|------|------|
| | | | | %C | %H | %N |
| 3a | 0,72 | (C ₄₈ H ₃₀ N ₄ O ₆ S · H ₂ O) _n (808,88) | Calc. | 71,27 | 3,99 | 6,93 |
| | | | Found | 70,60 | 3,77 | 6,86 |
| 3b | 1,10 | (C ₅₂ H ₃₈ N ₄ O ₆ S · H ₂ O) _n (864,98) | Calc. | 72,21 | 4,66 | 6,48 |
| | | | Found | 71,52 | 4,40 | 6,43 |
| 3c | 1,55 | (C ₅₃ H ₄₀ N ₄ O ₆ S · H ₂ O) _n (879,01) | Calc. | 72,42 | 4,82 | 6,37 |
| | | | Found | 72,37 | 4,28 | 5,85 |
| 3d | 1,72 | (C ₅₄ H ₄₂ N ₄ O ₆ S · H ₂ O) _n (893,04) | Calc. | 72,63 | 4,97 | 6,27 |
| | | | Found | 72,58 | 4,22 | 5,76 |
| 3e | 2,28 | (C ₅₅ H ₄₄ N ₄ O ₆ S · H ₂ O) _n (907,06) | Calc. | 72,83 | 5,11 | 6,18 |
| | | | Found | 72,93 | 4,74 | 6,05 |
| 3f | 2,73 | (C ₅₆ H ₄₆ N ₄ O ₆ S · H ₂ O) _n (921,09) | Calc. | 73,02 | 5,25 | 6,08 |
| | | | Found | 72,58 | 5,06 | 6,10 |
| 3g | 1,33 | (C ₅₈ H ₅₀ N ₄ O ₆ S · H ₂ O) _n (949,14) | Calc. | 73,40 | 5,52 | 5,90 |
| | | | Found | 73,53 | 5,24 | 5,76 |
| 3h | 0,80 ^{c)} | (C ₅₂ H ₃₀ N ₄ O ₆ S · H ₂ O) _n (856,92) | Calc. | 72,89 | 3,76 | 6,54 |
| | | | Found | 72,20 | 3,76 | 6,38 |
| 3i | 1,02 ^{d)} | (C ₅₂ H ₃₀ N ₄ O ₆ S · 2H ₂ O) _n (874,94) | Calc. | 71,38 | 3,92 | 6,40 |
| | | | Found | 71,95 | 3,29 | 6,24 |
| 3j | 1,14 | (C ₅₉ H ₄₈ N ₄ O ₆ S · 2H ₂ O) _n (977,16) | Calc. | 72,52 | 5,36 | 5,73 |
| | | | Found | 72,82 | 4,95 | 5,55 |
| 3k | 1,31 ^{d)} | (C ₅₉ H ₃₆ N ₄ O ₆ S · H ₂ O) _n (947,04) | Calc. | 74,83 | 4,04 | 5,92 |
| | | | Found | 74,43 | 3,91 | 5,47 |
| 3l | 1,72 ^{d)} | (C ₅₈ H ₃₄ N ₄ O ₇ S · 2H ₂ O) _n (967,04) | Calc. | 72,04 | 3,96 | 5,79 |
| | | | Found | 72,46 | 3,70 | 5,92 |
| 3m | 2,01 | (C ₅₈ H ₃₄ N ₄ O ₇ S · 2H ₂ O) _n (967,04) | Calc. | 72,04 | 3,96 | 5,79 |
| | | | Found | 72,43 | 3,26 | 5,55 |
| 3n | 2,58 | (C ₆₄ H ₃₈ N ₄ O ₈ S · 2H ₂ O) _n (1 059,13) | Calc. | 72,59 | 3,99 | 5,29 |
| | | | Found | 72,61 | 3,60 | 5,18 |
| 3o | 2,29 | (C ₆₄ H ₃₈ N ₄ O ₈ S · H ₂ O) _n (1 041,11) | Calc. | 73,84 | 3,87 | 5,38 |
| | | | Found | 73,16 | 3,49 | 5,11 |

a) Polymerization was carried out with 1,25 mmol of each monomer, 0,8 mL of triphenyl phosphite, 1,6 mL of pyridine, and 0,8 g of CaCl₂ in 8 mL of *N*-methyl-2-pyrrolidone (NMP) at 100 °C for 3 h under nitrogen.

b) Measured at 30 °C with a concentration of 0,5 g/dL in *N,N*-dimethylacetamide (DMAc) containing 5 wt.-% LiCl unless otherwise indicated.

c) Measured in conc. H₂SO₄.

d) Measured at 30 °C with a concentration of 0,5 g/dL in *N*-methyl-2-pyrrolidone (NMP).

Properties of polymers

Tab. 3 shows the qualitative solubility of poly(amide-imide)s in various solvents. Almost all aliphatic-aromatic poly(amide-imide)s, **3a–g** and **3j**, were highly soluble in a variety of organic solvents including amide-type solvents such as NMP and DMAc, *m*-cresol and pyridine. The solubility behavior of the wholly aromatic poly(amide-imide)s **3h, i, k–o** is quite different from that of the aliphatic-aromatic ones and reveals

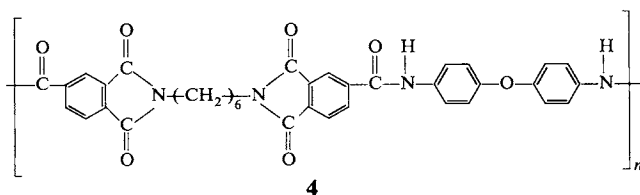
Tab. 3. Solubilities of poly(amide-imide)s **3a–o**^{a)}

| Polymer | Solvent ^{b)} | | | | | | |
|-----------|-----------------------|-----|-----|------|----|------------------|----------------------|
| | DMAc | DMF | NMP | DMSO | Py | <i>m</i> -Cresol | DMAc/ 5 wt.-%LiCl |
| 3a | ++ | s | ++ | -- | ++ | ++ | ++ |
| 3b | ++ | s | ++ | -- | s | ++ | ++ |
| 3c | ++ | s | ++ | -- | ++ | ++ | ++ |
| 3d | ++ | s | ++ | -- | ++ | ++ | ++ |
| 3e | s | s | ++ | -- | ++ | ++ | ++ |
| 3f | ++ | s | ++ | -- | ++ | ++ | ++ |
| 3g | ++ | s | ++ | -- | ++ | ++ | ++ |
| 3h | -- | -- | +- | -- | -- | -- | +- |
| 3i | +- | -- | ++ | +- | -- | -- | ++ |
| 3j | ++ | +- | ++ | -- | -- | ++ | ++ |
| 3k | -- | -- | ++ | +- | -- | -- | s |
| 3l | -- | -- | ++ | -- | -- | -- | s |
| 3m | +- | ++ | ++ | -- | -- | -- | ++ |
| 3n | +- | +- | ++ | -- | s | -- | ++ |
| 3o | -- | -- | ++ | -- | -- | s | ++ |

^{a)} ++: soluble; --: insoluble; +-: partially soluble; s: swelling.

^{b)} DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; NMP: *N*-methyl-2-pyrrolidone; DMSO: dimethyl sulfoxide; Py: pyridine.

less solubility in polar amide-type solvents. Almost all of them are only soluble in NMP but insoluble in pyridine and *m*-cresol. Polymer **3h** with the *p*-phenylene unit between the imide rings showed the least solubility. All the polymers are insoluble in common organic solvents such as tetrahydrofuran, chloroform, acetone, and benzene; however, they are all soluble in concentrated sulfuric acid. In general, the aliphatic-aromatic poly(amide-imide)s showed better solubility than their homologs with other diamine moieties as described in our previous publication⁷⁾. For example, polymer **4** derived from diimide-diacid **2d** and 4,4'-oxydianiline was insoluble in all the organic solvents



listed in Tab. 3 and showed some degree of crystallinity as evidenced by the X-ray diffraction pattern. The increase of the solubility is apparently attributable to the incorporation of the bulky pendant tetraphenylthiophene moiety into the polymer backbone which hinders a close packing of the polymer chains. However, the smaller solubility of the wholly aromatic poly(amide-imide)s, despite the presence of bulky, pendant phenyl groups, is an unexpected result.

The X-ray diffraction patterns of the poly(amide-imide)s indicated that all the polymers were amorphous, possibly due to the presence of bulky, pendant phenyl groups of the tetraphenylthiophene moieties. Strong, transparent and flexible films could be cast from the DMAc solutions of aliphatic-aromatic poly(amide-imide)s and from the NMP solutions for other wholly aromatic polymers. The tensile properties of some typical poly(amide-imide)s are summarized in Tab. 4. The films had tensile

Tab. 4. Tensile properties of poly(amide-imide) films^{a)}

| Polymer | Strength at yield in MPa | Strength at break in MPa | Elongation to break in % | Initial modulus in GPa |
|------------------------|--------------------------|--------------------------|--------------------------|------------------------|
| 3b | — | 81 | 13 | 2,19 |
| 3c | — | 71 | 30 | 1,89 |
| 3d | 78 | 74 | 22 | 1,91 |
| 3e^{b)} | 106 | 119 | 73 | 2,25 |
| 3f | — | 65 | 18 | 1,54 |
| 3g | 63 | 65 | 23 | 1,45 |
| 3m^{b)} | 134 | 128 | 23 | 3,17 |
| 3n^{b)} | 98 | 126 | 66 | 2,51 |
| 3o^{b)} | — | 89 | 68 | 2,45 |

a) Films were cast from polymer solutions of *N,N*-dimethylacetamide (DMAc) unless otherwise indicated.

b) Cast from polymer solutions of *N*-methyl-2-pyrrolidone (NMP).

strengths of between 65 and 128 MPa, elongations to break of between 13 and 73%, and initial moduli of between 1,45 and 3,17 GPa. Some polymer films such as those from **3d**, **e**, **g–n** behave as a ductile materials with a yield point and moderate elongation to break.

The thermal behavior of the polymers was characterized using differential scanning calorimetry (DSC) and thermogravimetry (TG). Fig. 2 shows typical TG curves of some

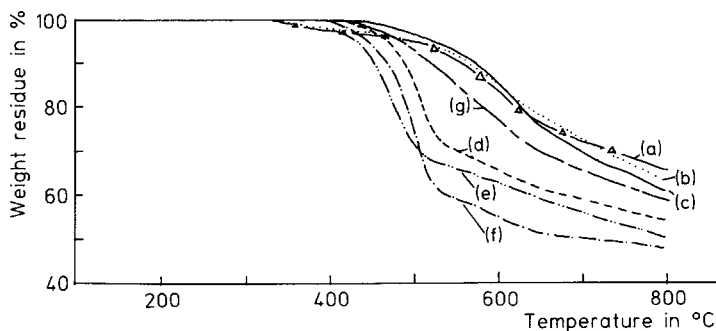


Fig. 2. Thermogravimetry curves of poly(amide-imide)s **31** (a), **3k** (b), **3n** (c), **3b** (d), **3j** (e), **3g** (f), and **3a** (g), with a heating rate of 20 °C/min in nitrogen

poly(amide-imide)s with a heating rate of 20 °C/min under flowing nitrogen. The thermogravimetric traces indicate that all the poly(amide-imide)s possess moderately high thermal stability with no significant weight loss up to temperatures of approximately 400 °C in a nitrogen atmosphere. The thermal behavior data of all poly(amide-imide)s are summarized in Tab. 5. The 10% weight-loss temperatures were recorded in the range of between 414 and 550 °C in air and between 451 and 578 °C in nitrogen. The presence of an aliphatic chain in the polymer backbone led to a lower initial decomposition temperature and rapid decomposition around 450–550 °C. Wholly aromatic poly(amide-imide)s **3h**, **i**, **k–o** evidently show higher thermal stability and undergo extensive carbonization upon non-oxidative degradation leaving high char yields up to 67 wt.-% at 800 °C.

Tab. 5. Thermal properties of poly(amide-imide)s **3a–o**

| Polymer | $T_g / ^\circ\text{C}^{\text{a}}$ | Decomposition temperature in $^\circ\text{C}^{\text{b}}$ | | Char yield ^{c)} in wt.-% |
|-----------|-----------------------------------|--|-------------|--------------------------------------|
| | | in air | in nitrogen | |
| 3a | — ^{d)} | 448 | 517 | 58,3 |
| 3b | 242 | 439 | 486 | 53,8 |
| 3c | 240 | 451 | 482 | 55,6 |
| 3d | 234 | 445 | 488 | 62,7 |
| 3e | 227 | 440 | 473 | 52,5 |
| 3f | 220 | 414 | 467 | 56,0 |
| 3g | 203 | 440 | 480 | 47,8 |
| 3h | — | 507 | 564 | 67,3 |
| 3i | — | 521 | 578 | 61,8 |
| 3j | — | 459 | 451 | 50,0 |
| 3k | — | 549 | 560 | 62,2 |
| 3l | — | 549 | 556 | 65,1 |
| 3m | — | 520 | 573 | 59,1 |
| 3n | — | 517 | 568 | 60,9 |
| 3o | — | 550 | 554 | 54,7 |

a) Glass transition temperature from differential scanning calorimetry (DSC) measurements conducted at a heating rate of 20 °C/min in nitrogen.

b) Temperature at which 10% weight loss was recorded with thermogravimetry (TG) at a heating rate of 20 °C/min.

c) Char yield at 800 °C in nitrogen.

d) No discernible transition was observed in the differential scanning calorimetry (DSC) traces.

Tab. 5 also summarizes the thermal transition data of the poly(amide-imide)s. DSC measurements were conducted with a heating rate of 20 °C/min. Quenching from the elevated temperatures to room temperature in air yields more amorphous samples so that in most cases the glass transition temperatures (T_g) could be easily measured in the second-heating traces of DSC. The T_g of most wholly aromatic poly(amide-imide)s were not obtained through DSC; however, almost all poly(amide-imide)s containing aliphatic chains showed clear glass transitions T_g in their second DSC heating

traces. For the aliphatic-aromatic poly(amide-imide)s, T_g 's were lowered with increasing length of the methylene segment, and the values were in the range of between 203 and 242 °C for polymers **3b–g**. Polymer **3a** with two methylene groups in the repeating unit showed no discernible transition in the DSC curve. Well-defined melting points of the polymers could not be detectable through DSC, due to their amorphous nature as evidenced by the X-ray diffraction measurements.

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