3053

# Poly(amide-imide)s prepared from 4,4'-[1,4(or 1,3)-phenylenebis(isopropylidene-1,4-phenyleneoxy)]dianiline, trimellitic anhydride, and various aromatic diamines

*Sheng-Huei Hsiao\*, Chin-Ping Yang, Jr-Chen Fan*

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

SUMMARY:
Two imide ring-bearing dicarboxylic acids, *N,N'*-[1,4(or 1,3)-phenylenebis(isopropyl-idene-1,4-phenyleneoxy-1,4-phenylene)]diphthalimide-4-carboxylic acid (*p*-**4** and *m*-**4**), were prepared via condensation of 4,4'-[1,4(or1,3)-phenylenebis(isopropylidene-1,4-pheny-leneoxy)]dianiline (*p*-**3** and *m*-**3**) with trimellitic anhydride. Two series of novel poly(amide-imide)s were synthesized by the direct polycondensation of the diimide-diacids *p*-**4** and *m*-**4**, respectively, with various aromatic diamines using triphenyl phosphite and pyridine as condensing agents. The inherent viscosities of the resultant poly(amide-imide)s were in the range of 0,43 – 1,68 dL/g, and most of these polymers were amorphous, as revealed by wide-angle X-ray diffractograms. Almost all the poly(amide-imide)s were readily soluble in polar aprotic solvents such as *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), and *N,N*-dimethylformamide (DMF), and could be solution-cast into transparent, flexible, and tough films. These polymers had glass transition temperatures in the range of 200 – 267 °C and showed no significant decomposition below 450 °C, with 10% weight loss being recorded above 485 °C in nitrogen or air.

## Introduction

Aromatic polyimides are of industrial interest because they exhibit high thermal stability with good mechanical and electrical performance over a wide temperature range as well as excellent solvent resistance. However, their applications have been limited owing to their poor solubility and intractable characteristics. To overcome these disadvantages, some copolymers have been proposed, in particular poly(amide-imide)s. Because of containing both amide and imide groups in polymer repeating units, poly(amide-imide)s have properties between polyamides and polyimides; accordingly, this class of polymers offers a good compromise between excellent thermal stability and processability.

Aromatic poly(amide-imide)s were usually prepared from trimellitic anhydride (TMA) or its acyl chloride with aromatic diamines or diisocyanates[1–5]. Some years ago, we have successfully applied the phosphorylation reaction[6] to the direct synthesis of high-molecular-weight poly(amide-imide)s from the TMA-derived imide ring-bearing dicarboxylic acids and aromatic diamines using triphenyl phosphite and pyridine as condensing agents[7–12]. This route provides significant advantages in manufacturing operations compared with conventional methods.

In one of our recent publications[13], we successfully synthesized a series of poly(amide-imide)s based on the diimide-diacid condensed from TMA and 4,4'-[isopropyl-

idenebis(1,4-phenyleneoxy)]dianiline, a diamine containing one isopropylidene and two aryl ether linkages between the phenyl units. The results of thermal analyses and solubility test of these polymers proved that incorporation of isopropylidene and aryl ether groups could impart processability to the polymer, with only limited reduction of thermal stability. As a follow-up to this work, we were interested in exploring another series of novel poly(amide-imide)s which were synthesized from $N,N'$-[1,4(or 1,3)-phenylenebis(isopropylidene-1,4-phenyleneoxy-1,4-phenylene]diphthalimide-4-carboxylic acid ($p$-4 and $m$-4), a diimide-diacid containing two isopropylidene and two aryl ether linking groups between the phenylene units, and various aromatic diamines. We expect that the processability, e. g., the melt viscosity and solubility, of the poly-(amide-imide)s would be further promoted by inserting additional isopropylidene and phenylene groups because of the dilution of the phthalimide groups in the polymer chain.

## Experimental part

### Materials and measurements

4,4'-(1,4-Phenylenediisopropylidene)diphenol ($p$-1) and 4,4'-(1,3-phenylenediisopropylidene)diphenol ($m$-1) were used as received from Mitsui Petrochemical Ind. (Japan). Hydrazine monohydrate (from Wako), $p$-chloronitrobenzene (from TCI), 10% palladium on charcoal (Pd/C; from Fluka), and trimellitic anhydride (from Wako) were also used without previous purification.

$p$-Phenylenediamine (5a) (TCI) and $m$-phenylenediamine (5b) (TCI) were vacuum-distilled before use. The other aromatic diamines, 2,4-tolylenediamine (5c) (TCI), benzidine (5d) (TCI), 4,4'-methylenedianiline (5e) (TCI), 4,4'-oxydianiline (5f) (TCI), 3,4'-oxydianiline (5g) (Mitsui Toatsu), 4,4'-thiodianiline (5h) (TCI), 4,4'-(1,4-phenylenedioxy)dianiline (5i) (TCI), 4,4'-(1,3-phenylenedioxy)dianiline (5j) (Chriskev), were of high purity when received from the manufacturers and used without any further purification. According to the reported method [14], 4,4'-[isopropylidenebis(1,4-phenyleneoxy)]dianiline (5k), 4,4'-[sulfonylbis(1,4-phenyleneoxy)]dianiline (5l), 4,4'-[perfluoroisopropylidenebis(1,4-phenyleneoxy)]dianiline (5m), and 4,4'-[1,4(or 1,3)-phenylenebis(isopropylidene-1,4-phenyleneoxy]dianiline ($p$-3 and $m$-3) were prepared by the nucleophilic substitution reaction of $p$-chloronitrobenzene and the corresponding bisphenols followed by catalytic hydrazine reduction.

Commercially obtained anhydrous calcium chloride was dried under vacuum at 180 °C for 10 h. N-Methyl-2-pyrrolidone (NMP), $N,N$-dimethylacetamide (DMAc), $N,N$-dimethylformamide (DMF), and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP; from TCI) was purified by distillation under reduced pressure.

The measurements were performed as outlined in our previous publication [15].

### Synthesis of diimide-diacids p-4 and m-4

$N,N'$-[1,4-phenylenebis(isopropylidene-1,4-phenylenoxy-1,4-phenylene)]diphthalimide-4-carboxylic acid (p-4): Ten gram (0,019 mol) of $p$-3 and 7,3 g (0,038 mol) of trimellitic anhydride were dissolved in 60 mL of dried DMF at 60 °C. Then, 60 mL of toluene was added, and the mixture was heated at reflux temperature until about 0,7 mL of water was distilled off azeotropically. On cooling, the reaction solution was poured in distilled water,

and the resulting solid product, collected by filtration, was washed thoroughly with methanol. This product was dried and then recrystallized from DMF to give diimide-diacid p-**4** in quantitative yield; m.p. 335−337 °C.

IR (KBr): 3200−3700 cm$^{-1}$ (carboxylic acid, —OH), 1700 cm$^{-1}$ (carboxylic acid, C=O), 1781, 1719 cm$^{-1}$ (imide, C=O), 729 cm$^{-1}$ (imide ring).

$C_{54}H_{40}N_2O_{10}$ (876,93)    Calc.    C 73,96    H 4,60    N 3,19
                                     Found    C 73,09    H 4,67    N 3,88

*m*-**4** was synthesized from *m*-**3** and TMA in a similar manner; m.p. 288−290 °C.

$C_{54}H_{40}N_2O_{10}$ (876,93)    Calc.    C 73,96    H 4,60    N 3,53
                                     Found    C 73,40    H 4,58    N 3,53

*Polycondensation*

A typical example of polycondensation was as follows: A mixture of 1,096 g (1,25 mmol) of diimide-diacid p-**4**, 0,1352 g (1,25 mmol) of *m*-phenylenediamine (**5 b**), 0,36 g of calcium chloride, 0,9 mL of TPP, 1,4 mL of pyridine, and 4 mL of NMP was heated with stirring at 105 °C for 3 h. As the polycondensation proceeded, the solution became gradually viscous. The obtained polymer solution was trickled into 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, and the inherent viscosity of the polymer in DMAc containing 5 wt.-% LiCl was 0,62 dL/g, measured at a concentration of 0,5 g/dL at 30 °C.

IR (film): 3300, 1676 and 1545 cm$^{-1}$ (amide), 1779 and 1725 cm$^{-1}$ (imide, C=O), 725 cm$^{-1}$ (imide ring deformation).

$(C_{60}H_{44}N_4O_8)_n$ (949,04)$_n$    Calc.    C 75,94    H 4,67    N 5,90
                                          Found    C 74,14    H 4,76    N 5,76

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

**Results and discussion**

*Monomer synthesis*

The diamines 4,4'-[1,4(or 1,3)-phenylenebis(isopropylidene-1,4-phenyleneoxy)]dianiline (*p*- or *m*-**3**) were prepared by a nucleophilic substituiton of 4,4'-[1,4(or 1,3)-phenylenediisopropylidene]diphenol (*p*-**1** or *m*-**1**) with *p*-chloronitrobenzene in the presence of $K_2CO_3$ and then reduced. The dicarboxylic acids *p*-**4** and *m*-**4** with two preformed imide rings were derived from diamine *p*-**3** or *m*-**3** and trimellitic anhydride via a two-stage procedure that included ring-opening addition in polar solvents like DMF to give the intermediate amic acid, followed by cyclodehydration to the imido-dicarboxylic acid by means of toluene-water azeotropic distillation (*Scheme 1*).

The yields of diamine compounds and diimide-diacid monomers were high, and their structures were confirmed by elemental analysis and IR spectra. The IR spectrum of the diimide-diacid monomer *p*-**4** showed characteristic imide absorption peaks at 1781, 1719 and 725 cm$^{-1}$, assigned to symmetrical and asymmetrical C=O stretch-
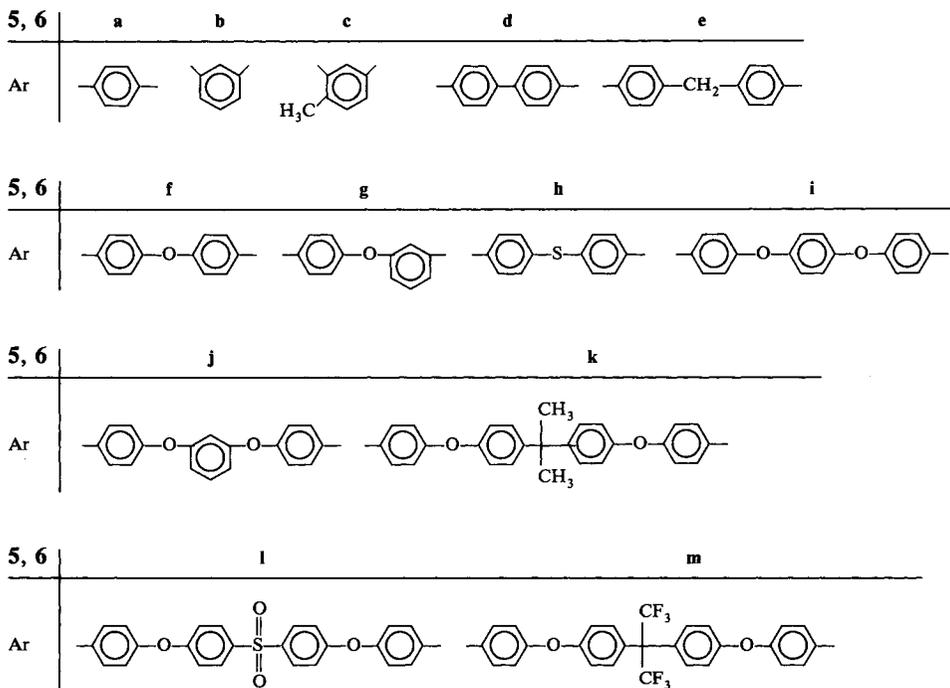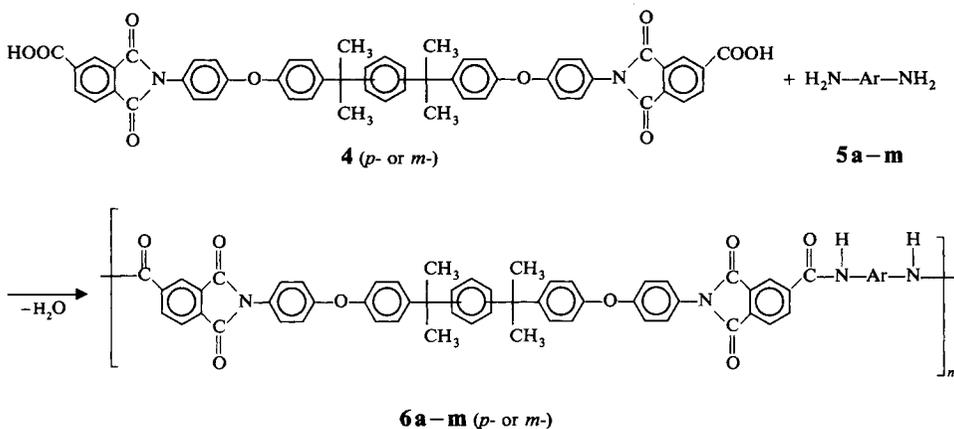
*Scheme 1:*



**1** (*p*- or *m*-)



**2** (*p*- or *m*-)



**3** (*p*- or *m*-)





**4** (*p*- or *m*-)
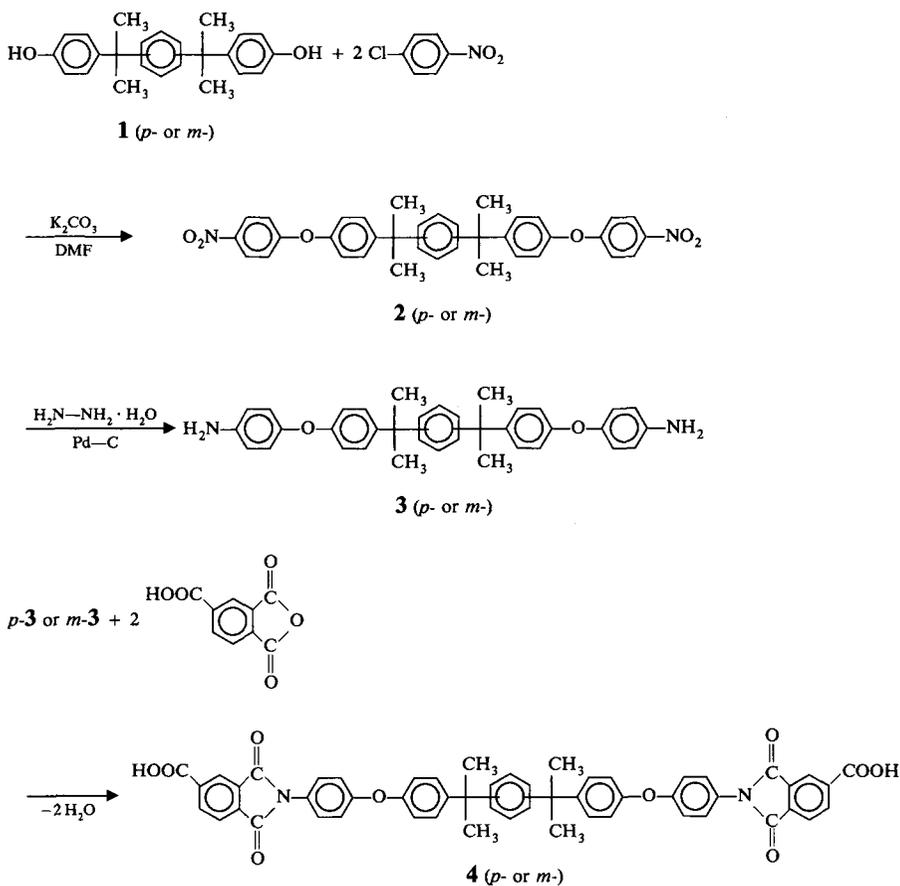
ing and imide ring deformation, respectively, together with characteristic carboxylic acid absorptions near $3200-3700$ cm$^{-1}$ (—OH) and $1700$ cm$^{-1}$ (C=O).

*Polymer synthesis*

Two series of novel poly(amide-imide)s (*p*-**6a-m** and *m*-**6a-m**) containing isopropyl-idene and aryl ether units were prepared by the direct polycondensation of diimide-diacids *p*-**4** and *m*-**4** with various aromatic diamines, respectively, using triphenyl phosphite and pyridine as condensing agents (*Scheme 2*). Almost all the reactions proceeded readily in homogeneous solution and gave quantitative yields of polymers. As shown in Tab. 1, these polymers were synthesized with moderate to high inherent viscosities of $0,43-1,68$ dL/g in DMAc 5 wt.-% LiCl. Their weight-average molecular

*Scheme 2:*

HOOC ... C=O, N—⟨benzene⟩—O—⟨benzene⟩—C(CH₃)(CH₃)—⟨benzene⟩—C(CH₃)(CH₃)—⟨benzene⟩—O—⟨benzene⟩—N ... C=O, COOH   + H₂N—Ar—NH₂

**4** (*p*- or *m*-)                                                      **5a–m**

−H₂O →

[ ... C=O, C=O, N—⟨benzene⟩—O—⟨benzene⟩—C(CH₃)(CH₃)—⟨benzene⟩—C(CH₃)(CH₃)—⟨benzene⟩—O—⟨benzene⟩—N ... C=O, C=O, C—N(H)—Ar—N(H) ]ₙ

**6a–m** (*p*- or *m*-)

| 5, 6 | a | b | c | d | e |
|---|---|---|---|---|---|
| Ar | –⟨C₆H₄⟩– | ⟨C₆H₄⟩ | H₃C–⟨C₆H₃⟩ | –⟨C₆H₄⟩–⟨C₆H₄⟩– | –⟨C₆H₄⟩–CH₂–⟨C₆H₄⟩– |

| 5, 6 | f | g | h | i |
|---|---|---|---|---|
| Ar | –⟨C₆H₄⟩–O–⟨C₆H₄⟩– | –⟨C₆H₄⟩–O–⟨C₆H₄⟩– | –⟨C₆H₄⟩–S–⟨C₆H₄⟩– | –⟨C₆H₄⟩–O–⟨C₆H₄⟩–O–⟨C₆H₄⟩– |

| 5, 6 | j | k |
|---|---|---|
| Ar | –⟨C₆H₄⟩–O–⟨C₆H₄⟩–O–⟨C₆H₄⟩– | –⟨C₆H₄⟩–O–⟨C₆H₄⟩–C(CH₃)(CH₃)–⟨C₆H₄⟩–O–⟨C₆H₄⟩– |

| 5, 6 | l | m |
|---|---|---|
| Ar | –⟨C₆H₄⟩–O–⟨C₆H₄⟩–SO₂–⟨C₆H₄⟩–O–⟨C₆H₄⟩– | –⟨C₆H₄⟩–O–⟨C₆H₄⟩–C(CF₃)(CF₃)–⟨C₆H₄⟩–O–⟨C₆H₄⟩– |

weight ($\overline{M}_w$) estimated by GPC curves relative to standard polystyrene were in the range of 75300–152300, the $\overline{M}_w/\overline{M}_n$ values were between 1,56–2,83. Because of insolubility in DMF containing 0,01 mol-% LiBr, the eluent of GPC measurement, the

molecular weight values of the poly(amide-imide)s $p$-**6a**, $p$-**6d**, $m$-**6a**, and $m$-**6d** could not be determined. All other poly(amide-imide)s were of sufficiently high molecular weight to permit casting to tough films.

The IR spectrum of poly(amide-imide) showed characteristic bands for amide groups at 3300, 1676, and 1545 cm$^{-1}$, assignable to N—H stretching, C=O stretching, and N—H bending, respectively. The primary absorption bands for imide groups also appeared in the spectrum around 1780, 1725, and 725 cm$^{-1}$. All the poly(amide-imide)s were also subjected to elemental analysis. In all cases however, the carbon percentages were found to be lower than the calculated ones for the proposed structures. This is possibly caused by the hygroscopic nature of the amide groups of these polymers.

*Properties of polymers*

The qualitative solubility of the poly(amide-imide)s was tested in various solvents.

Except for the polymers $p$-**6a**, $p$-**6d**, $m$-**6a**, and $m$-**6d** derived from $p$-phenylenediamine or benzidine, all the poly(amide-imide)s were readily soluble in amide-type polar solvents such as DMAc, DMF, and NMP. In addition, these polymers were also completely soluble in $m$-cresol, but they showed less solubility in DMSO and THF. The good solubility is apparently due to the combined favorable effects of arylene ether and isopropylidene linkers in the trimellitimide-based poly(amide-imide) main chain.

Except for polymers $m$-**6a** and $m$-**6d**, all other polymers exhibit amorphous patterns in wide-angle X-ray diffractograms. The semi-crystalline nature of the polymers $m$-**6d** may be attributable to their rigid structure caused by the benzidine moiety and resulted in insolubility in polar solvents as mentioned above, which is in agreement with the general rule that the solubility decreases with increasing crystallinity. Although poly-(amide-imide)s $p$-**6a** and $p$-**6d** also showed poor solubility in organic solvents, their X-ray diffractograms did not reveal strong reflection peaks. With the exception of polymers $p$-**6a**, $p$-**6d**, $m$-**6a**, and $m$-**6d**, all other polymers can be solution-cast into transparent, flexible, and tough films. The films had tensile strength of 53 – 80 MPa, elongation to break of 5 – 30%, and initial modulus of 1,36 – 1,87 GPa. Some films yielded during the tensile test.

The thermal behaviour of the polymers was characterized by means of differential scanning calorimetry (DSC) and thermogravimetry (TG). As a representative example, poly(amide-imide) $p$-**6a** obtained from diimido-diacid $p$-**4** and $p$-phenylenediamine (**5a**) exhibited a rapid weight loss between 480 and 580 °C; however, the rate of thermal decomposition in air was slightly lower than in nitrogen, presumably due to oxidation or some oxidative crosslinking of the polymer chains. At temperatures over 600 °C, the rate of decomposition began to slow down in nitrogen and left 55,7 wt.-% of char residue at 800 °C; on the contrary, the polymer still rapidly decomposed in air and completely degraded near 800 °C. All other poly(amide-imide)s showed a similar thermal behavior with no significant loss up to 450 °C in air or nitrogen.

The thermal properties of the poly(amide-imide)s are summarized in Tab. 1. These polymers lost 10% weight at temperatures in the range of 493 – 527 °C in nitrogen and 485 – 535 °C in air, and left 46,8 – 63,5% char residue at 800 °C in nitrogen. Tab. 1 also

Tab. 1.  Characteristics of poly(amide-imide)s[a]

| Polymer | $\eta_{inh}$[b] dL/g | $\bar{M}_w$[c] $\times 10^{-4}$ | $\bar{M}_w/\bar{M}_n$ | $T_g/°C$[d] | $T_d/°C$[e] in air | in N$_2$ | Residual wt.-% at 800 °C in N$_2$ |
|---|---|---|---|---|---|---|---|
| p-6a | 0,58 | — | — | 255 | 513 | 505 | 55,7 |
| p-6b | 0,62 | 11,63 | 2,83 | 267 | 519 | 512 | 61,0 |
| p-6c | 1,07 | 10,89 | 1,63 | 255 | 495 | 506 | 62,0 |
| p-6d | 0,43 | — | — | —[f] | 531 | 525 | 60,0 |
| p-6e | 0,57 | 7,53 | 2,17 | 255 | 514 | 496 | 59,0 |
| p-6f | 0,68 | 8,43 | 2,65 | 253 | 501 | 494 | 57,5 |
| p-6g | 0,81 | 11,44 | 1,99 | 260 | 517 | 513 | 60,8 |
| p-6h | 0,49 | 7,81 | 1,56 | 256 | 510 | 493 | 60,1 |
| p-6i | 0,65 | 8,81 | 1,66 | 246 | 523 | 509 | 58,2 |
| p-6j | 0,65 | 11,05 | 1,76 | 225 | 524 | 527 | 63,5 |
| p-6k | 0,62 | 10,68 | 1,70 | 236 | 519 | 513 | 60,2 |
| p-6l | 0,64 | 12,94 | 1,67 | 264 | 510 | 508 | 56,1 |
| p-6m | 0,51 | 10,10 | 1,57 | 242 | 519 | 519 | 56,8 |
| m-6a | 0,69 | — | — | 210 | 485 | 515 | 52,6 |
| m-6b | 1,68 | 14,02 | 1,85 | 227 | 523 | 523 | 62,7 |
| m-6c | 0,61 | 12,81 | 2,27 | 222 | 511 | 504 | 55,2 |
| m-6d | 0,44 | — | — | 218[g] | 539 | 524 | 46,8 |
| m-6e | 0,78 | 12,37 | 1,77 | 215 | 526 | 514 | 60,5 |
| m-6f | 0,97 | 15,23 | 1,81 | 215 | 518 | 521 | 62,1 |
| m-6g | 0,81 | 12,11 | 1,73 | 214 | 526 | 525 | 61,5 |
| m-6h | 0,86 | 12,28 | 1,75 | 219 | 514 | 505 | 60,8 |
| m-6i | 0,89 | 11,44 | 2,07 | 207 | 524 | 521 | 58,9 |
| m-6j | 0,84 | 12,50 | 1,81 | 200 | 521 | 522 | 59,0 |
| m-6k | 0,81 | 11,64 | 1,74 | 211 | 524 | 517 | 58,9 |
| m-6l | 0,89 | 14,14 | 1,79 | 227 | 514 | 520 | 53,8 |
| m-6m | 0,74 | 13,65 | 1,88 | 215 | 529 | 524 | 54,7 |

[a]  Polymerization was carried out with 1,25 mmol of each monomer, 0,9 mmol of TPP, 1,4 mL of pyridine, and 0,36 g of CaCl$_2$ in 4 mL of NMP at 105 °C for 3 h.

[b]  Inherent viscosity measured at a concentration of 0,5 g/dL in DMAc containing 5 wt.-% LiCl dissolved, at 30 °C.

[c]  Determined by GPC.

[d]  Glass transition temperature from the second heating traces of DSC measurements conducted at a heating rate of 20 °C/min in nitrogen.

[e]  Decomposition temperature at which 10% weight loss was recorded with thermogravimetry (TG) at a heating rate of 20 °C/min.

[f]  Difficult to judge.

[g]  With a melting endothermic peak at 329 °C in the first heating trace of DSC.

gives the glass transition temperatures ($T_g$'s) of the polymers. These polymers had $T_g$'s over 200 °C. Except for polymer p-6d, all other polymers showed a clear glass transition in the range of 200–267 °C on the second heating trace after quenching the samples from elevated temperatures. It is reasonable that poly(amide-imide)s p-6a-m possess 25 to 45 °C higher glass transition temperatures compared with their corre-

sponding *m*-isomers, *m*-6a – m. This phenomenon would be associated with the fact that the *meta*-oriented phenylene ring disrupts the linear conformation, thus reducing the chain rigidity of the polymer chain.

[1] Y. Imai, N. Maldar, M. Kakimoto, *J. Polym. Sci., Polym. Chem. Ed.* **23**, 2077 (1985)

[2] A. Ray, Y. V. Rao, V. K. Bhattacharya, S. Maiti, *Polym. J. (Tokyo)* **15**, 169 (1983)

[3] J. de Abajo, J. P. Gabarda, J. Fontan, *Angew. Makromol. Chem.* **71**, 143 (1978)

[4] J. L. Nieto, J. G. de la Campa, J. de Abajo, *Makromol. Chem.* **183**, 557 (1982)

[5] M. Kakimoto, R. Akiyama, Y. Negi, Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.* **26**, 99 (1988)

[6] N. Yamazaki, M. Matsumoto, F. Higashi, *J. Polym. Sci., Polym. Chem. Ed.* **13**, 1373 (1975)

[7] C.-P. Yang, S.-H. Hsiao, *Makromol. Chem.* **190**, 2119 (1989)

[8] C.-P. Yang, J.-M. Cheng, S.-H. Hsiao, *Makromol. Chem.* **191**, 155 (1990)

[9] C.-P. Yang, J.-H. Lin, S.-H. Hsiao, *J. Polym. Sci., Part A: Polym. Chem.* **29**, 1175 (1991)

[10] C.-P. Yang, S.-H. Hsiao, J.-H. Lin, *J. Polym. Sci., Part A: Polym. Chem.* **30**, 1865 (1992)

[11] C.-P. Yang, W.-T. Chen, *Makromol. Chem.* **194**, 1993 (1993)

[12] C.-P. Yang, W.-T. Chen, *J. Polym. Sci., Part A: Polym. Chem.* **31**, 3081 (1993)

[13] C.-P. Yang, S.-H. Hsiao, J.-H. Lin, *J. Polym. Sci., Part A: Polym. Chem.* **31**, 2995 (1993)

[14] K. Suematsu, *Macromolecules* **18**, 2085 (1985)

[15] S.-H. Hsiao, C.-P. Yang, J.-C. Fan, *Macromol. Chem. Phys.* **196**, 3041 (1995)