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Synthesis and properties of new soluble poly(amide-imide)s from 3,3′,5,5′-tetramethyl-2,2-bis[4-(4-trimellitimidophenoxy)phenyl]propane with various diamines

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Abstract

A series of new soluble poly(amide-imide)s were prepared from the diimide-dicarboxylic acid, 3,3′,5,5′-tetramethyl-2,2-bis[4-(4-trimellitimidophenoxy)phenyl]propane (TBTPP), with various diamines by the direct polycondensation in *N*-methyl-2-pyrrolidinone using triphenyl phosphite and pyridine as condensing agents. The new diimide-dicarboxylic acid TBTPP bearing isopropylidene and methyl-substituted arylene ether units was synthesized by the condensation reaction of 3,3′,5,5′-tetramethyl-2,2-bis[4-(4-aminophenoxy)phenyl]propane with trimellitic anhydride. All the polymers were obtained in quantitative yields with inherent viscosities of 0.58-1.03 dl g^{-1}. The polymers were amorphous and most of them were readily soluble in aprotic polar solvents such as *N*-methyl-2-pyrrolidinone, *N*,*N*-dimethylacetamide, and *N*,*N*-dimethylformamide, as well as in less polar solvents such as dimethyl sulfoxide, *m*-cresol, pyridine and γ-butyrolactone, and also even in tetrahydrofuran. The glass transition temperatures of the polymers were determined by the differential scanning calorimetry (DSC) method and were in the range 240–278°C. These polymers were stable up to 450°C and lose 10% weight in the range of 454–484°C and 448–482°C in nitrogen and oxygen, respectively. The polymer films had a tensile strength range of 98–122 MPa and a initial modulus range of 2.7–3.8 GPa. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: 3,3′,5,5′-tetramethyl-2,2-bis[4-(4-trimellitimidophenoxy)phenyl]propane (TBTPP); Poly(amide-imide)s; Direct polycondensation

1. Introduction

There is a growing interest in poly(amide-imide)s (PAIs) for a variety of applications as they retain good mechanical properties at high temperatures and show easier processability when compared with other aromatic thermostable polymers [1–3].

PAIs are usually prepared by low-temperature polycondensation of an aromatic diamine with the acyl chloride of trimellitic anhydride [4–6] or with acyl chlorides of aromatic diacids containing performed imide rings [7–11]. The former method requires a high temperature or chemical cyclodehydration step of the poly(amic acid) formed, while the second requires a two-step synthesis of diacyl chloride monomers.

Recently the triphenyl phosphite (TPP) and pyridine promoted polycondensation of diamines with bistrimellitimides [12–16] or with *N*-carboxyphenyl trimellitimides [17,18] have been an important achievement in the synthesis of PAIs. This direct polycondensation route avoids using moisture-sensitive acid chlorides and provides significant advantages in manufacturing operations compared with conventional methods. In addition, this synthetic route to PAIs can offer us the option of introducing specific functionality between amide or imide groups. Several attempts have been made to modify the PAIs structure by introducing the functional groups or substituents capable of reducing the chain rigidity and further increasing their tractability [13–18].

In previous articles [19,20] we described new soluble polyimides and polyamides based on the new diamine, 3,3′,5,5′-tetramethyl-2,2-bis[4-(4-aminophenoxy)phenyl]-propane (TBAPP), bearing isopropylidene and methyl-substituted arylene ether units. It was found, in fact, that incorporation of these flexible linkages into the polymer backbone reduces the crystallinity, and enhances the solubulity and melt-moldability of the polymers. In addition, the methyl substituent on phenylene also effectively enhances the solubility and thermo-oxidative stability of polymers. In our continuing effort to develop easily processable high-performance polymers which have good solubility and

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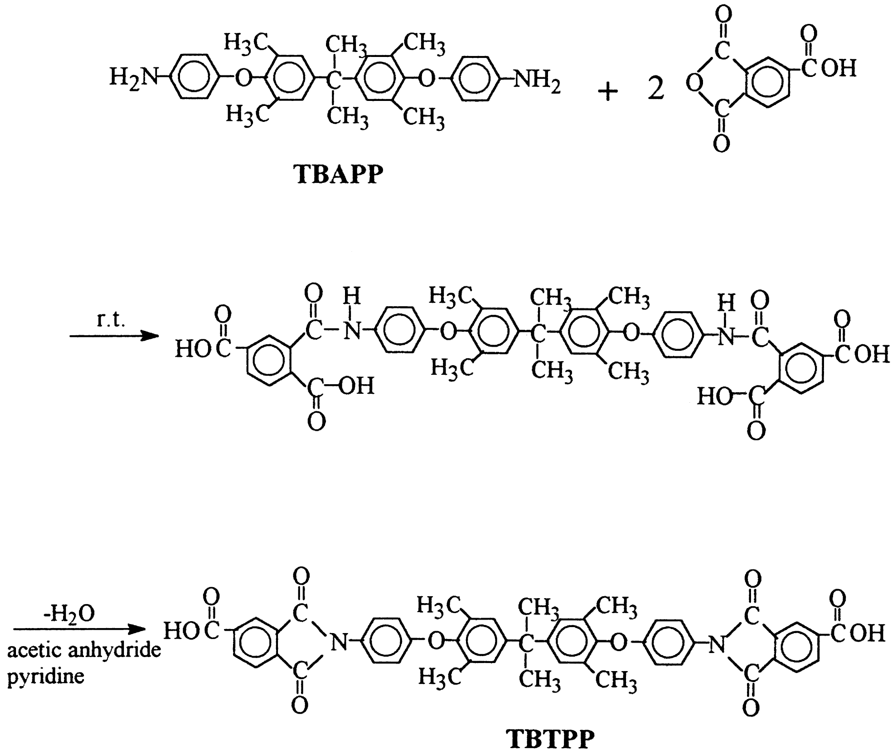


Scheme 1.

thermo-oxidative stability, we prepared a series of new highly soluble poly(amide-imide)s herein.

The PAIs have been prepared by direct polycondensation of various diamine with a new diimide-dicarboxylic acid, 3,3′,5,5′-tetramethyl-2,2-bis[4-(4-trimellitimidophenoxy)-phenyl]propane (TBTPP), condensed from TBAPP and trimellitic anhydride. The solubility, crystallinity thermal properties and tensile properties of the PAIs are investigated in this article.

2. Experimental

2.1. Materials

Trimellitic anhydride was purified by sublimation. *N*-Methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc) and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Acetic anhydride was purified by vacuum distillation. 2,2-Bis[4-(4-aminophenoxy)phenyl] propane (DA1), 2,2-bis[4-(4-aminophenoxy)-phenyl]hexafluoropropane (DA2), 1,4-bis(4-amino-phenoxy)benzene (DA4), and 4,4′-bis(4-aminophenoxy)biphenyl (DA7) were supplied from Wakayama Seika Co. Ltd and used without further purification. 3,3′,5,5′-Tetramethyl-2,2-bis[4-(4-aminophenoxy)phenyl]propane (TBAPP), 3,3′,5,5′-tetramethyl-bis[4-(4-aminophenoxy)phenyl]sulfone (DA3), 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene (DA5), 1,4-bis(4-aminophenoxy)-2,5-di-*tert*-butylbenzene (DA6) and 2,2′-dimethyl-4,4′-bis(4-aminophenoxy)biphenyl (DA8) were synthesized and purified according to the method previously reported [19,21–24].

2.2. Monomer synthesis

2.2.1. 3,3′,5,5′-tetramethyl-2,2-bis[4-(4-trimellitimidophenoxy)phenyl]propane (TBTPP)

A flask was charged with 1.60 g (3.45 mmol) of TBAPP, 1.36 g (7.14 mmol) of trimellitic anhydride, and 7 ml of DMAc. The mixture was stirred at room temperature for 5 h under argon atmosphere. To the solution was added 4 ml of acetic anhhydride and 2.5 ml of pyridine with stirring at room temperature for 1 h and then the mixture was refluxed for 4 h. A yellowish precipitate which formed upon cooling was filtered off, washed several times with methanol, and purified by recrystallization with DMAc/water mixture.

Yield: 86%, mp 242–243°C.

ANAL. calculated for $C_{49}H_{38}O_{10}N_2$: C, 72.23%; H, 4.70%; N, 3.44%; found: C, 72.35%; H, 4.63%; N, 3.47%.

2.3. Polymer synthesis

2.3.1. Synthesis of polymer PAI-1

A mixture of 0.267 g (0.65 mmol) of diamine DA1, 0.5296 g (0.65 mmol) of TBTPP, 0.25 g of calcium chloride, 0.7 ml of triphenyl phosphite, 0.6 ml of pyridine, and 2.5 mL of NMP was refluxed for 3 h. After cooling, the

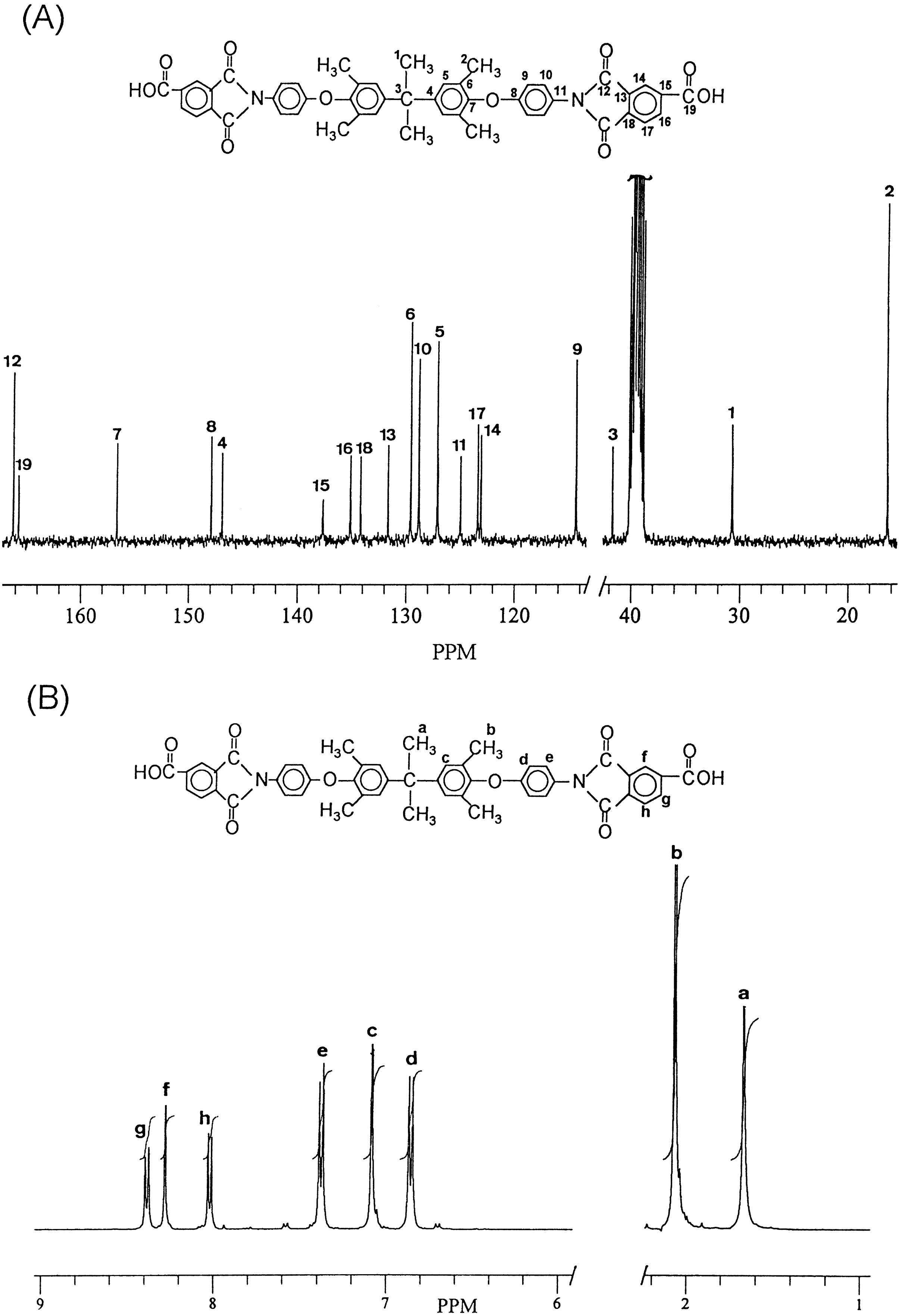
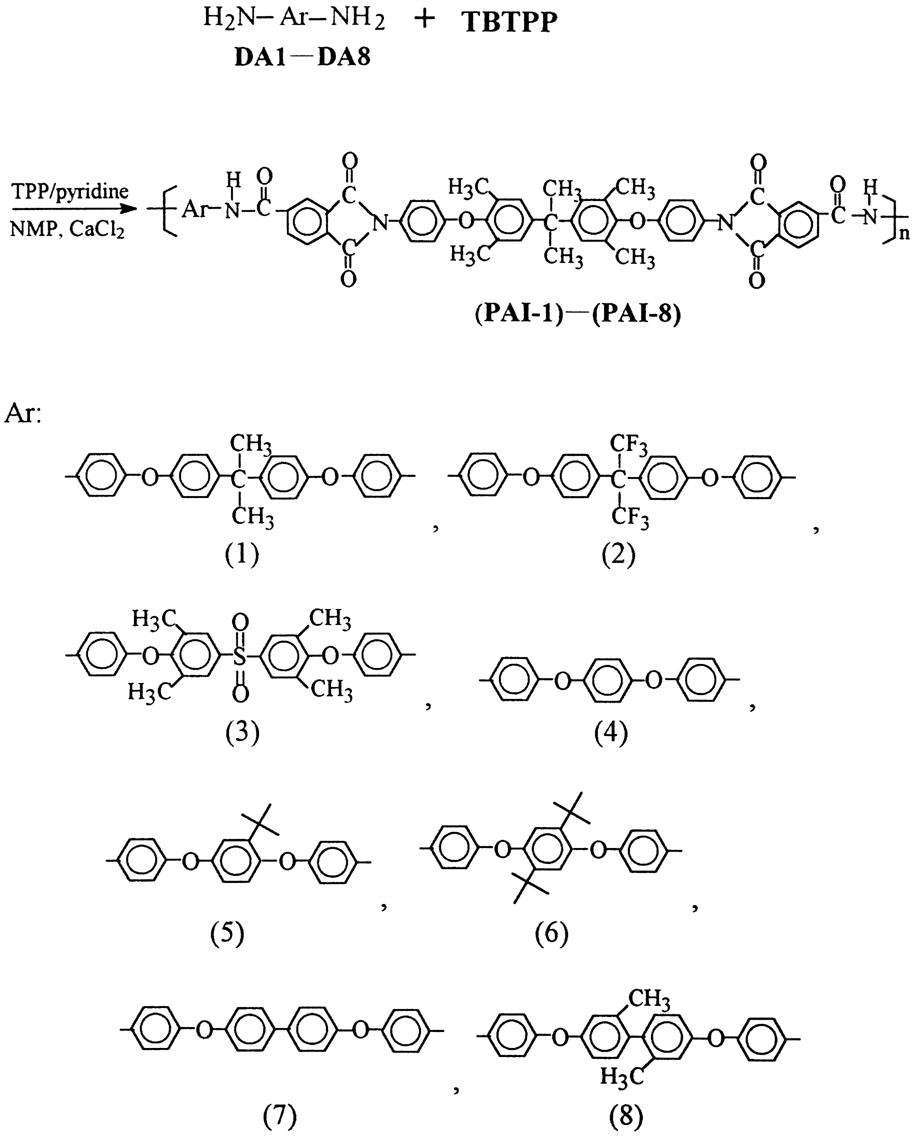


Fig. 1. N.m.r. spectra of TBTPP. Use DMSO-d_6 as solvent: (A) ^{13}C n.m.r.; and (B) ^{1}H n.m.r.



Scheme 2.

reaction mixture was poured into a large amount of methanol with constant stirring, producing a stringy precipitate that was washed thoroughly with methanol and hot water, collected on a filter, and dried at 100°C under vacuum. The inherent viscosity of the polymers in DMAc was 0.61 dl g^{-1}, measured at a concentration 0.5 g dl^{-1} at 30°C. All other PAIs were prepared analogously.

2.4. Measurements

The inherent viscosities of all polymers were measured at 0.5 g dl^{-1} in DMAc using a Ubbelohde viscometer. Elemental analysis was made on a Perkin-Elmer 2400 instrument. ^{13}C and ^{1}H n.m.r. spectra were obtained in DMSO-d_6 using a Jeol EX-400 operating at 399.65 MHz for carbon and 100.40 MHz for proton. Wide-angle X-ray diffraction patterns were performed at room temperature with film specimens on an X-ray diffractometer (Philips model PW 1710) using Ni filtered Cu-Kα radiation (30 kV, 25 mA). Thermogravimetric data were obtained on a Du Pont 2100 in flowing nitrogen or oxygen (60 cm^3 min^{-1}) at a heating rate of 20°C min^{-1}. Differential scanning calorimetry (DSC) analysis was performed on a Du Pont 2100 differential scanning calorimeter. Mechanical properties were determined from stress–strain curves obtained with a Orientec Tensilon with a load cell of 10 kg. A gauge of 3 cm and a strain rate of 2 cm min^{-1} were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and ca. 0.05 mm thick).

Table 1
Inherent viscosity and solubility of PAIs

Polymer	η_{inh}[a] (dl g^{-1})	Solubility[b]								
		NMP	DMAc	DMF	DMSO	*m*-Cresol	Pyridine	γ-Butyrolactone	THF	Chloroform
PAI-1	0.61	+	+	+	+	+	+	+	+	±
PAI-2	0.58	+	+	+	+	+	+	+	+	±
PAI-3	1.03	+	+	+	±	+	+	+	+	±
PAI-4	0.67	+	+	+	+	+	+	+	+	–
PAI-5	0.61	+	+	+	+	+	+	+	+	±
PAI-6	0.66	+	+	+	±	+	+	+	+	±
PAI-7	0.97	+	+	+	±	+	+	+	+	–
PAI-8	0.83	+	+	+	+	+	+	+	+	±

[a] Inherent viscosity measured at a concentration of 0.5 g dl^{-1} in DMAc at 30°C.
[b] Solubility: +, soluble at room temperature; ±, partial soluble; −, insoluble.

3. Results and discussion

3.1. Synthesis of monomer

The diimide-dicarboxylic acid monomer TBTPP containing isopropylidene and methyl-substituted arylene ether units was obtained according to the route illustrated in Scheme 1. It was prepared from TBAPP and trimellitic anhydride by refluxing in DMAc, using acetic anhydride and pyridine as condensing agents. The diimide-dicarboxylic acid monomer could be purified by recrystallization up to the purity degree required for polycondensation. The new monomer was characterized by elemental analysis, ir and n.m.r. spectroscopy. The ir spectrum of TBTPP showed absorption bands appearing at 3460 (acid –OH), 1769 (symmetric imide C=O stretching), 1715 (acid C=O stretching and asymmetric imide C=O stretching), 1374 (imide ring vibration, axial), and 725 cm^{-1} (imide ring vibration, out-of-plane), confirming the presence of imide rings in the structure. On the other hand, the C–O–C stretching band was observed at 1223 cm^{-1}. The detailed structure assignments of the ^{13}C and ^{1}H n.m.r. spectra are presented and identified in Fig. 1(A and B). The positions of chemical shift for each carbon and proton were readily assigned as shown in these figures. However, the protons for the acid group of TBTPP in the ^{1}H n.m.r. spectrum was not observed. This was probably due to the fast exchange of this proton with a trace amount of moisture associated with the solvent [12]. The diamine monomers used in the synthesis of PAIs were commercially available (DA1, DA2, DA4 and DA5), while the others were prepared according to previously reported procedures [21–24].

3.2. Synthesis of the PAIs

The use of the TPP/pyridine system as a condensing agent for dicarboxylic acids and aromatic diamines to form amide bonds is an efficient way to obtain polyamides of moderate polymerization degree on a laboratory scale [25,26]. This method has been used in the preparation of PAIs from diimide-dicarboxylic acid (TBTPP) and various diamines, and yielding alternating (amide–amide)-(imide–imide) links in the polymer backbone (Scheme 2). The PAIs were obtained in almost quantitative yields, and had inherent viscosity values ranging between 0.58 and 1.03 dl g^{-1}. These are reported in Table 1 along with the solubilities in various solvents. The molecular structure of PAIs was checked by elemental analysis and ir spectroscopy. The elemental analysis correlated sufficiently with the supposed structure. Specifically, the ir spectrum of PAI-1 showed characteristic absorptions of imide groups at 1770, 1717 and 1375 cm^{-1}, and those of the amide group at 3338 and 1668 cm^{-1}.

3.3. Properties of polymers

Table 1 summarizes the solubility of these PAIs. Remarkably, all these PAIs were easily soluble at room temperature in aprotic polar solvents such as NMP, DMAc, and *N*,*N*-dimethylformamide (DMF), as well as in less polar solvents such as *m*-cresol, pyridine and γ-butyrolactone, and also even in tetrahydrofuran (THF). The improved solubility of these PAIs as compared with that of related PAIs can be explained by the presence of tetramethyl substituents on the phenylene unit [15]. Due to these units, the packing of macromolecular chains in tight structures through hydrogen bonding between amide groups is probably disturbed and, consequently, the solvent molecules can penetrate easily to solubilize the chains. Mohanty et al. [27] had reported that the tetramethyl substituents on the phenylene unit would make the polymer less polar in nature, indicating that the methyl substituted arylene would effectively enhance the solubility of the polymer.

The wide-angle X-ray diffraction patterns of PAIs indicated that the polymer films were amorphous. This result could be explained in terms of the presence of the flexible isopropylidene and ether groups, which reduced the rigidity of the polymer chain. In addition, methyl groups on the phenylene also inhibited close packing of the polymer chains [19,20]. The X-ray results were consistent with that of the solubility behavior of the resulting polymers.

Table 2
Mechanical properties of PAIs

Polymer code	Tensile strength (MPa)	Elongation at break (%)	Initial modulus (GPa)
PA1-1	122	6	3.5
PAI-2	109	5	2.7
PAI-3	118	7	3.3
PAI-4	98	5	2.8
PAI-5	106	8	3.0
PAI-6	110	8	2.9
PAI-7	109	6	3.2
PAI-8	102	4	3.8

All the PAIs possess outstanding film-forming properties. Transparent flexible films have been obtained by casting polymer solution from DMAc onto glass plates, followed by gradually heating up to 150°C under vacuum to remove the solvent. Even the polymer PAI-2 which has the lowest viscosity gave quite flexible film. This can be explained by the flexibilizing effect of isopropylidene and ether bridges present in the main chain. The mechanical properties such as tensile strength, elongation at break and initial modulus of the PAIs films are collected in Table 2. The polymer films exhibit a high tensile strength and tensile modulus above 98 MPa and 2.8 GPa, respectively, indicating that they are strong materials.

The thermal properties of PAIs were investigated by means of differential scanning calorimetry (DSC) as well as thermogravimetric analysis (TGA), and the thermal data are summarized in Table 3.

There is no melting endotherm present in the DSC thermograms, which is consistent with the amorphous nature of the PAIs. The glass transition temperature (T_g), determined in second heating runs of DSC measurements, of the investigated PAIs was in the range of 240–278°C. Some structure–properties relations can be inferred from these data. The presence of the flexible isopropylidene and perfluoroisopropylidene [-C(CF_3)$_2$-] in the diamine moiety of the PAIs (PA-1 and PAI-2) lowers the glass transition temperature of the polymers. As can be expected, the sulfone-containing PAI-3 exhibited the highest T_g due to its higher intermolecular force [28]. Notably, polymer PAI-6 having two *tert*-butyl substituents gives a higher T_g than PAI-5 which has only one *tert*-butyl substituent. This is due to the former containing symmetric di-*tert*-butyl substituents appearing to pack efficiently (perhaps better than expected) while polymer containing unsymmetric mono *tert*-butyl substituent packs quite loosely [22,23]. The replacement of the phenylene unit (PAI-4) with the biphenylylene unit (PAI-7) increases the chain rigidity, thus increasing the T_g.

All the synthesized PAIs showed good resistance to thermal degradation in a nitrogen and oxygen atmosphere. They did not in fact show significant weight loss up to temperatures close to 450°C, and the T_d values (temperatures which correspond to a 10% weight loss) range from 454 to 484°C and from 448 to 482°C in nitrogen and oxygen, respectively. Most of the PAIs had similar T_d values in nitrogen and oxygen, indicating that PAIs based on TBTPP showed thermooxidative stability in O_2. An analogous behavior has been observed for polyimides and polyamides derived from diamine TBAPP [18,19]. For all polymers the residual weights at 800°C in nitrogen are still higher than 46%. A comparison of the T_g and T_d values indicates the PAIs possess a wide ‘processing window’, T_d–T_g, and, therefore, suggests easy melt processability.

Table 3
Thermal properties of PAIs

Polymer code	T_g[a] (°C)	T_d (°C)[b]		Char yield[c] (%)
		In N_2	In O_2	
PAI-1	240	480	461	54
PAI-2	243	482	480	60
PAI-3	278	454	448	46
PAI-4	249	479	471	60
PAI-5	242	478	471	57
PAI-6	260	480	451	54
PAI-7	262	484	482	58
PAI-8	258	480	478	60

[a] Glass transition temperature (T_g) measured on DSC at a heating rate of 20°C min^{-1}.

[b] Temperature at 10% weight loss recorded on TG at a heating rate of 20°C min^{-1}.

[c] Residual weight % at 800°C in nitrogen.

4. Conclusions

The new diimide-dicarboxylic acid monomer TBTPP which has isopropylidene and methyl-substituted arylene ether units can be prepared in high purity and yields. A series of amorphous and highly soluble PAIs can be obtained by the direct polycondensation of TBTPP with various diamines. These poly(amide–imide)s having good mechanical properties and high thermal stability were successfully synthesized.

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