

Synthesis and properties of polyamides based on a spirobichroman bis(ether-carboxylic acid)

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SUMMARY:

High molar-mass aromatic polyamides were obtained from 7,7'-bis(4-carboxyphenoxy)-4,4,4',4'-tetramethyl-2,2'-spirobichroman, a novel dicarboxylic acid monomer, by direct polycondensation reaction in *N*-methyl-2-pyrrolidone (NMP) with various aromatic diamines, using triphenyl phosphite and pyridine as condensing agents. Polyamides having inherent viscosities of 0.73–1.08 dL/g were obtained in quantitative yield. All the polyamides, even that derived from benzidine, are completely amorphous and readily soluble in a variety of organic solvents such as NMP, *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and *m*-cresol. Their solutions can be cast into transparent, flexible and tough films. All the polyamides show distinct glass transitions in the range of 182–235 °C on their differential scanning calorimetry (DSC) traces. The 10% weight loss temperatures in nitrogen and air are above 416 and 422 °C, respectively.

Introduction

Wholly aromatic polyamides (aramids) are thermally stable polymers with an attractive combination of chemical, physical, and mechanical properties^{1,2}. For example, poly(*p*-phenyleneterephthalamide) and poly(*m*-phenyleneisophthalamide), commercially known as Kevlar and Nomex, exhibit a number of useful properties such as thermal stability, chemical resistance, and low flammability coupled with excellent mechanical properties in the form of fibers. On the other hand, their use in some applications is prevented due to their poor processability caused by limited solubility in most organic solvents and by high glass-transition or melting temperatures. Thus, considerable research has been carried out aimed at developing aramids that have better processability while retaining their outstanding thermal and mechanical properties.

The introduction of flexible groups and/or thermally stable bulky groups in the polymer backbone have been general approaches to change the chemical structure of polyamides^{3–10}. Generally, the modified aromatic polyamides are prepared using diamine or diacid monomers incorporating a flexible group and/or bulky unit. Many useful bis(ether amine)s^{7–12} and bis(ether carboxylic acid)s^{13–15}, which can be readily synthesized from the bisphenol precursors, have been demonstrated in literature.

7,7'-Dihydroxy-4,4,4',4'-tetramethyl-2,2'-spirobichroman (TMSBC-diol), an aromatic diol having an interesting structure 1 as shown in Scheme 1, can be easily prepared from acid-catalyzed cyclocondensation of resorcinol and acetone^{16,17}, and now is commercially available. Photographic films made from the polyesters derived from this diol have been described to exhibit improved physical properties such as high T_g and dimensional stability¹⁸. However, there is little published litera-

ture regarding the polymers based on this diol other than polyesters. The incorporation of a spiro structure into the polymer backbone would facilitate less intermolecular interaction and less probability of main chain scission due to the presence of multibonds and might increase main chain rigidity. Therefore, we considered it of interest to synthesize new polyamides based on diol **1**.

In this work, we will prepare a bis(ether carboxylic acid) (**3** in Scheme 1) from diol **1** and use this diacid to prepare polyamides bearing both ether group and bulky spirobichroman unit in the main chain. The solubility, film forming ability, crystallinity, tensile properties and thermal properties of these materials will also be investigated.

Experimental part

Materials

7,7'-Dihydroxy-4,4,4',4'-tetramethyl-2,2'-spirobichroman (**1**) (TCI) and *p*-fluorobenzonitrile (TCI) were used as received. *N,N*-Dimethylformamide (DMF; Wako) was purified by distillation under reduced pressure over calcium hydride. 4,4'-Bis(4-aminophenoxy)-biphenyl (**4g**; m. p. 198–199 °C) was prepared by the aromatic nucleophilic substitution reaction of 4,4'-biphenyldiol (Fluka) and *p*-chloronitrobenzene (TCI) in the presence of K₂CO₃, giving a bis(4-nitrophenoxy) compound, followed by catalytic hydrazine reduction¹⁹. *p*-Phenylenediamine (**4a**; TCI) and benzidine (**4c**; TCI) were purified by vacuum sublimation. *m*-Phenylenediamine (**4b**; Janssen) was purified by vacuum distillation. 4,4'-Oxydianiline (**4d**; TCI), 4,4'-methylenedianiline (**4e**; TCI), 1,4-bis(4-aminophenoxy)benzene (**4f**; TCI), 4,4'-diaminobenzanilide (**4h**; Chriskev) were used without purification. Calcium chloride was dried under vacuum at 180 °C for 8 h prior to use. *N*-Methyl-2-pyrrolidone (NMP; TCI) and pyridine (Wako) were distilled under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP; Wako) was purified by distillation under reduced pressure.

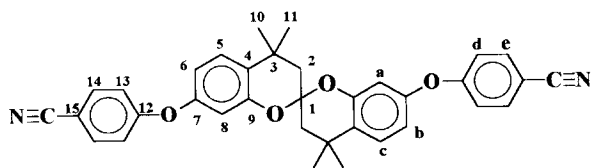
Synthesis of TMSBC-dinitrile **2**

TMSBC-diol **1** (25 g; 0,07 mol) was dissolved in a solution of DMF (70 mL) and toluene (70 mL) in a 500-mL round-bottomed flask equipped with a Dean-Stark trap. Anhydrous potassium carbonate (20 g; 0,14 mol) was added, and water was removed by azeotropic distillation with toluene. After water was removed completely, the residual toluene was distilled out from the system. After cooling the mixture to about 60 °C, *p*-fluorobenzonitrile (9 g; 0,07 mol) was added and the reaction mixture was continuously heated at 150 °C for 6 h. The mixture was allowed to cool and subsequently added to water (600 mL), to precipitate a white solid which was collected by filtration, washed repeatedly with methanol, and dried, to give 38,8 g (97%) of 7,7'-bis(4-cyanophenoxy)-4,4,4',4'-tetramethyl-2,2'-spirobichroman (**2**); m. p.: 215–216 °C.

IR (KBr): 2230 (C≡N str.), 1267, 1226 cm⁻¹ (C—O str.).

¹H NMR (CDCl₃): δ = 7,56 (d, H_c, 4H), 7,32 (d, H_c, 2H), 6,96 (d, H_g, 4H), 6,67, 6,65 (AB doublets, H_b, 2H), 6,39 (d, H_a, 2H), 2,14, 2,03 (AB doublets, —CH₂—, 4H), 1,58, 1,38 ppm (s, —CH₃, 12H).

¹³C NMR (CDCl₃): δ = 161,54 (C⁷), 153,32 (C¹²), 151,41 (C⁹), 134,04 (C¹⁴), 128,68 (C⁴), 127,82 (C⁵), 118,84 (C≡N), 117,75 (C¹³), 113,80 (C⁶), 109,44 (C⁸), 105,64 (C¹⁵), 98,43 (C¹), 46,31 (C²), 32,45, 32,23 (C¹⁰, C¹¹), 30,62 ppm (C³).



$C_{35}H_{30}N_2O_4$ (542.63)	Calc.	C 77,47	H 5,57	N 5,16
	Found	C 77,40	H 5,66	N 5,08

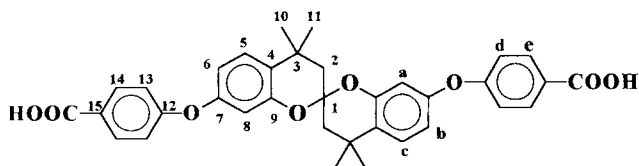
Synthesis of TMSBC-diacid **3**

In a 1-L flask were added dinitrile **2** (38,8 g, 0,07 mol), potassium hydroxide (81 g, 1,4 mol), and 1:1 volume mixture of water-ethanol (300/300 mL). The suspension was refluxed for 48 h to form a clear solution. The resulting hot clear solution was filtered to remove any insoluble impurities. After cooling, the filtrate was acidified by conc. HCl to pH = 3, and the white precipitate was collected by filtration, washed thoroughly with water, and dried in vacuo, to give 41,1 g (99%) of 7,7'-bis(4-carboxyphenoxy)-4,4,4',4'-tetramethyl-2,2'-spirobichroman (**3**); m.p.: 271–275 °C.

IR (KBr): 2500–3500 (broad, O–H str.), 1688 (C=O str.), 1265, 1224 cm^{-1} (C–O str.).

1H NMR (DMSO- d_6): δ = 7,93 (d, H_c , 4H), 7,45 (d, H_c , 2H), 6,99 (d, H_d , 4H), 6,70, 6,68 (AB doublets, H_b , 2H), 6,36 (d, H_d , 2H), 2,16, 2,03 (AB doublets, $-CH_2-$, 4H), 1,52, 1,33 ppm (s, $-CH_3$, 12H).

^{13}C NMR (DMSO- d_6): δ = 166,66 (C=O), 160,66 (C⁷), 153,84 (C¹²), 150,88 (C⁹), 131,53 (C¹⁴), 128,18 (C⁴), 127,74 (C⁵), 125,24 (C¹⁵), 117,19 (C¹³), 113,11 (C⁶), 108,03 (C⁸), 98,32 (C¹), 45,09 (C²), 31,96, 31,91 (C¹⁰, C¹¹), 30,05 ppm (C³).



$C_{35}H_{32}O_8$ (580,63)	Calc.	C 72,40	H 5,55
	Found	C 72,14	H 5,51

Polymerization

A typical polymerization process for polyamide **5a** is described as follows. In a 50-mL flask was added TMSBC-diacid **3** (1,25 mmol, 0,7258 g), *p*-phenylenediamine (1,25 mmol, 0,1351 g), calcium chloride (0,3 g), triphenyl phosphite (TPP, 0,9 mL), pyridine (0,8 mL), and NMP (2,5 mL). The mixture was stirred at 110 °C for 3 h. The resulting viscous reaction mixture was trickled slowly into stirring methanol, to precipitate white fibrous product which was washed thoroughly with methanol and hot water, collected by filtration, and dried. Yield: 0,82 g, 100%. This polymer had inherent viscosity of 0,74 dL/g, measured in DMAc-5 wt.-% LiCl at a concentration of 0,5 g/dL at 30 °C.

IR (film): 3312 (N–H str.), 1653 (C=O str.), 1263, 1226 cm^{-1} (C–O str.).

Other polyamides were prepared by a similar procedure.

Measurements

IR spectra were recorded on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. ^{13}C and ^1H NMR spectra were determined on a Jeol EX-400 NMR spectrometer with perdeuterodimethyl sulfoxide ($\text{DMSO}-d_6$) as an external reference and with tetramethylsilane (TMS) as an internal reference, respectively. The inherent viscosities were measured with a Cannon-Fenske viscometer thermostated at 30°C . Differential scanning calorimetry (DSC) analysis was performed on a Sinku Riko DSC-7000 coupled to a Sinku Riko TA-7000 thermal analyzer in flowing nitrogen ($30\text{ cm}^3/\text{min}$) at a heating rate of $10^\circ\text{C}/\text{min}$. Thermogravimetry (TG) was conducted with a Rigaku Thermoflex TG-8110 coupled to a Rigaku TAS-100 thermal analysis station. Measurements were performed with 9–11 mg sample heated in flowing nitrogen or air of $50\text{ cm}^3/\text{min}$ at a heating rate of $20^\circ\text{C}/\text{min}$. The wide-angle X-ray scattering measurements were carried out with a Rigaku Geiger Flex D-Max IIIa X-ray diffractometer, using Ni-filtered CuK_α radiation (40 kV, 15 mA) and a scanning rate of $2^\circ/\text{min}$. Tensile properties were determined from stress-strain curves obtained by an Instron Universal tester Model 1130 with a load cell of 5 kg. A gauge of 2 cm and a strain rate of 5 cm/min were used here. The measurements were made at room temperature using solution-cast 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.

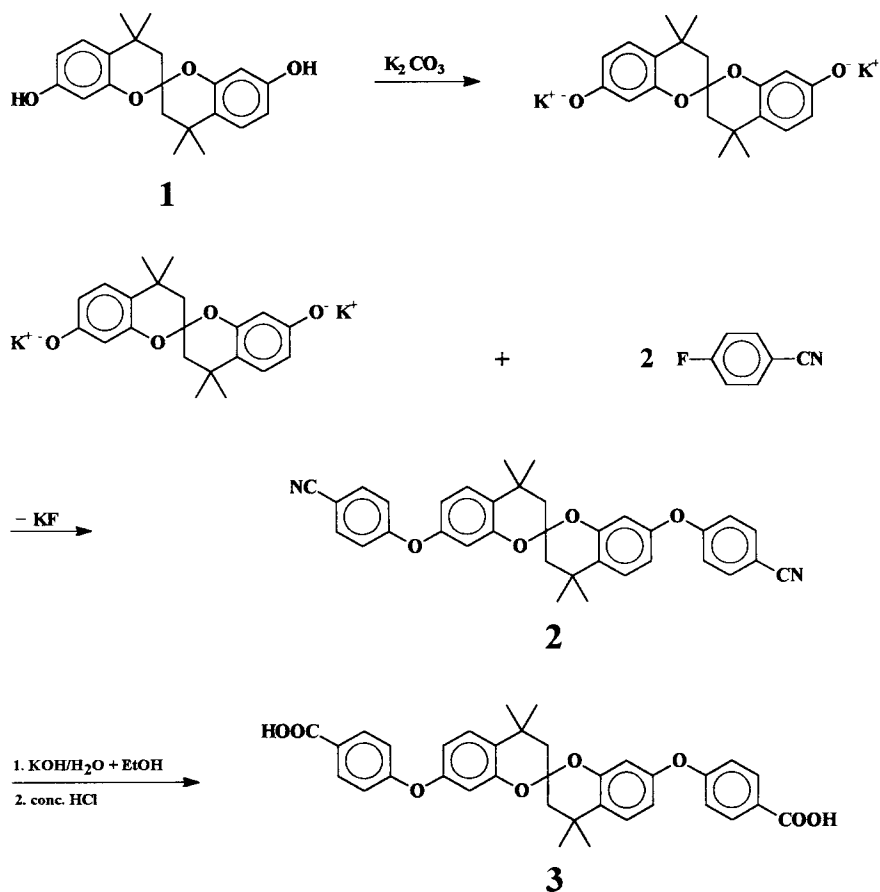
Results and discussion

Monomer synthesis

According to the synthetic route outlined in Scheme 1, TMSBC-diacid **3** was prepared in high yields through the aromatic nucleophilic displacement of the activated fluorine atoms of *p*-fluorobenzonitrile by the bisphenoxide ion of TMSBC-diol **1** followed by alkaline hydrolysis. The structures of compounds **2** and **3** were confirmed through elemental analysis and IR, ^1H , and ^{13}C NMR spectroscopy. When comparing the ^{13}C NMR spectra of TMSBC-dinitrile **2** and TMSBC-diacid **3**, it is found that the most obvious features are the shifts of the resonance signals for the cyano carbon and its adjacent carbon C^{15} . Because C^{15} in dinitrile **2** is shielded by the anisotropic field induced by the π electrons of $\text{C}\equiv\text{N}$, C^{15} resonates at higher field than the other aromatic carbons. After the cyano group was converted into the carboxyl group, the resonance peak of C^{15} moved to a lower field (from 105.64 to 125.24 ppm) due to the absence of anisotropic shielding, the original signal at 118.84 ppm assigned to cyano carbon disappeared, and the resonance of carbonyl carbon occurred at the farthest downfield (166.66 ppm).

Polymer synthesis

Polyamides **5a–h** were obtained by a Yamazaki-Higashi²⁰ phosphorylation polyamidation technique, i.e., they were prepared by direct polycondensation of TMSBC-diacid **3** with various aromatic diamines (**4a–h**) (Scheme 2) in NMP solutions containing dissolved CaCl_2 using TPP and pyridine as condensing agents. All the polycondensation reactions proceeded homogeneously throughout the reaction and resulted in highly viscous polymer solutions. The polyamides were isolated as

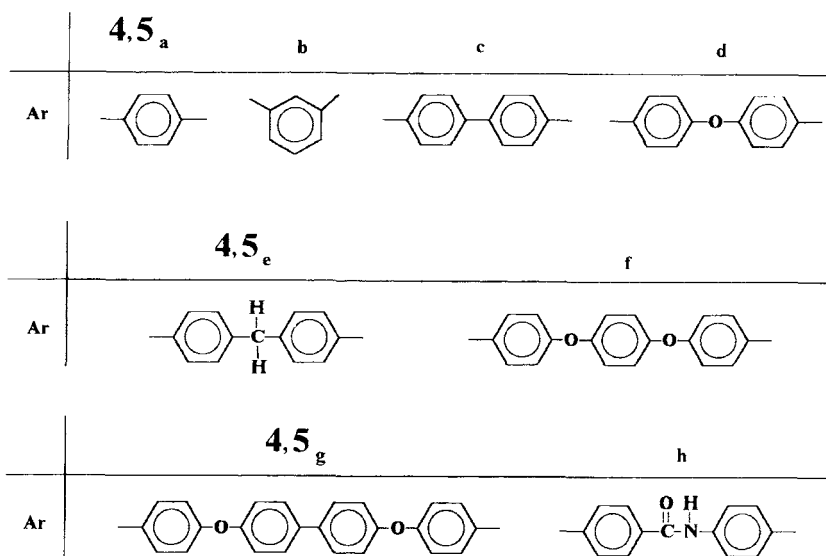
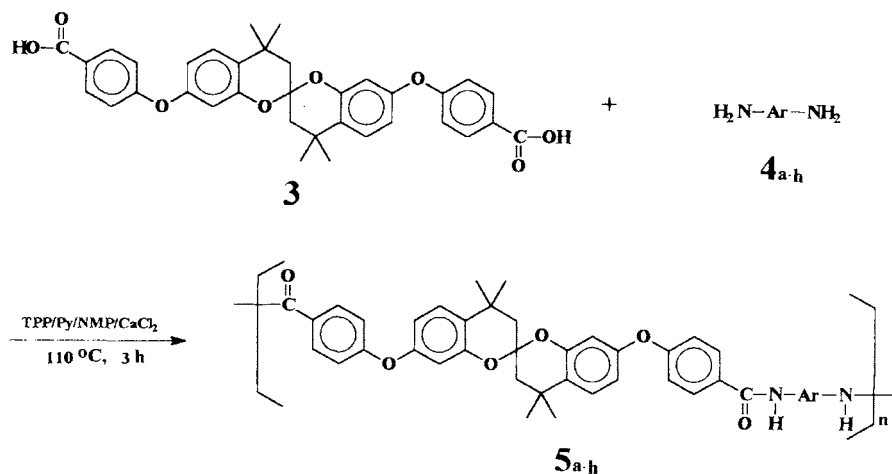
Scheme 1:

white fibers upon precipitation in methanol, and they had inherent viscosities of 0,73–1,08 dL/g (Tab. 1). The molecular structure of the polyamide was confirmed by IR spectroscopy. The IR spectrum shows characteristic bands at 3312 (N–H str.) and 1653 cm^{-1} (C=O str.) for amide group. Other characteristic vibrations include aliphatic C–H stretching at 2900 cm^{-1} , C–O–C stretching at 1200–1300 cm^{-1} , and aromatic C=C skeletal stretching at 1500 and 1600 cm^{-1} .

Properties of polymers

The crystallinity of the prepared polyamides was evaluated by wide-angle X-ray diffraction measurements. It is found that all the polyamides showed a completely amorphous diffraction pattern. It appears that the presence of diaryl ether kinks, together with the bulky nonlinear spirobichroman unit in the diacid moiety, leads to

Scheme 2:



loose chain packing. Due to the similar reason, all of these polyamides possess excellent solubility in organic solvents, in spite of the fact that some of them were derived from diamines with a more rigid structure such as *p*-phenylenediamine, benzidine, and 4,4'-diaminobenzanilide. All the polyamides are readily soluble in DMAc, NMP, DMF, and *m*-cresol, and most of them also in DMSO and THF.

All the polyamides could be solution-cast into flexible creasable films from the given solvents. These polyamide films have yield or tensile strengths in the range of 67–81 MPa and initial moduli in the 1.7–2.4 GPa range. Elongations to break are

relatively low (5–9%), except for the polymer based on 4,4'-bis(4-aminophenoxy)-biphenyl, which has an elongation of 25%.

The thermal properties of the obtained polyamides were investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC). Fig. 1 illustrates typi-

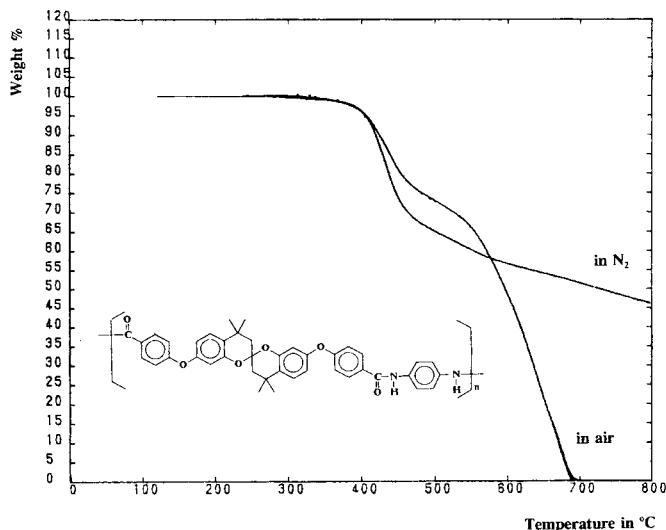


Fig. 1. TG curves of polyamide **5a** in air and nitrogen, with a heating rate of 20 °C/min

Tab. 1. Inherent viscosities and thermal properties of polyamides based on TMSBC-diacid

Polymer	$\eta_{inh}^a)$ dL/g	$T_g^b)$ in °C	Decomposition temperature ^{c)} in °C		Char yield ^{d)} in %
			in N ₂	in air	
5a	0,74	200	420	425	46,3
5b	0,79	194	423	426	44,4
5c	0,95	182	428	436	50,2
5d	0,92	190	427	422	53,5
5e	0,73	183	429	426	48,4
5f	0,78	194	434	435	49,5
5g	1,08	190	442	439	53,2
5h	0,97	235 (325, 365) ^{e)}	416	423	48,1

a) Measured at a concentration of 0,5 g/dL in DMAc-5 wt.-% LiCl at 30 °C.

b) Base line shift in the second heating DSC trace, with a heating rate of 10 °C/min in nitrogen.

c) Temperature at which 10% weight loss was recorded by TG at a heating rate of 20 °C/min.

d) Residual weight % at 800 °C in nitrogen.

e) Temperature at endothermic peak on the first DSC heating trace.

cal TG curves for the representative polyamide **5a** in both air and nitrogen atmosphere at a heating rate of 20°C/min. From these TG curves it may be deduced that the polymer is reasonably resistant to heat, since no significant weight loss occurred below 400°C. In nitrogen, about 46% weight residue remained even at 800°C, in contrast to the almost complete weight loss of the polymer when decomposed in air well below this temperature. However, presumably due to some oxidative crosslinking of aliphatic segments, the rate of thermal degradation in air was slightly lower than in nitrogen below 600°C. All other polyamides showed a similar thermal behavior, and all the polymers lost 10% weight above 416°C, with 44,4–53,5% char residue remaining at 800°C in nitrogen atmosphere (Tab. 1).

The glass transition temperatures (T_g) of the polyamides were determined from the DSC traces of samples that had been heated to 300°C and rapidly cooled prior to the run. The T_g was taken at the midpoint of the change in slope of the baseline in the second DSC heating trace. The DSC traces of all polyamides showed a strong baseline shift centred at 182–235°C. The highest T_g value was observed for polymer **5h** due to the presence of an amide linkage in the diamine residue which led to an increased intermolecular interaction. It can also be noted that there is a large window between the T_g and the decomposition temperature, which could be advantageous in the processing of these polymers.

Conclusions

A novel dicarboxylic acid monomer, 7,7'-bis(4-carboxyphenoxy)-4,4,4',4'-tetramethyl-2,2'-spirobichroman (TMSBC-diacid **3**), was prepared in high yields and high purity starting from 7,7'-dihydroxy-4,4,4',4'-tetramethyl-2,2'-spirobichroman and *p*-fluorobenzonitrile. A series of novel high-molar-mass polyamides have been synthesized by direct polycondensation of diacid **3** with various diamines by means of triphenyl phosphite and pyridine. Due to the presence of spirobichroman moieties in the main chain, these polymers are amorphous and readily soluble in a variety of organic solvents, which is very convenient for their processing. Free-standing films, which are very flexible and tough, have been obtained by casting polymer solutions onto glass substrates. They show a reasonable thermal stability and a large window between decomposition and glass transition temperatures. All these properties make these polymers potential candidates for high-performance thermoplastic materials.

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