Processable, high T_g polyimides containing benzimidazole moieties

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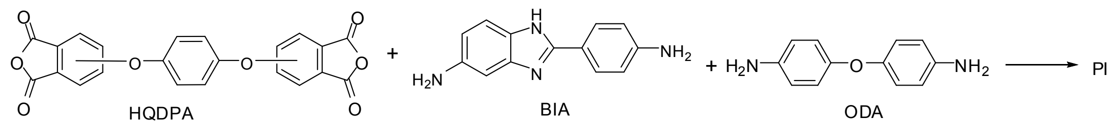
Aromatic polyimides (PI) have gained increasing attention owing to their unique features such as excellent mechanical properties, outstanding thermal-oxidative stabilities, superior chemical resistance as well as good dielectric performances and accordingly, these characteristic make it ideal for diverse applications such as aerospace, composite matrices and high performance materials [1]. However, most of the wholly aromatic PIs offer disadvantage of insolubility and difficult processing that confines their applications. To overcome these shortcomings, various structural modifications have been applied. Moreover, in advanced polymer composites there is a well-established need to produce polyimides that are cost-effective, processable and can withstand temperatures > 300 °C for extended periods of time. Therefore, there is a need to apply an adjusted degree of modification to optimize the balance of properties. Generally, it is noted that introduction of heterocyclic rings into the backbone of polyimide is helpful in substantial enhancement of mechanical and thermal properties [2]. Polybenzimidazoles (PBI), carrying hetero-aromatic benzimidazole ring (BI), are known to possess excellent thermal stability, good mechanical properties as well as good environmental resistance however their poor solution processability have restricted their practical use [3]. Benzimidazole with rigid rod like structure has gained attraction and employed as thermal-resistant monomer in high performance polyimides fabrication in past few decades [4-7]. However, to compensate the rigidity of benzimidazole units, many researchers copolymerized it with monomers containing flexible linkages with the purpose to tailor the properties of copolyimides.

Hence, to satisfy specific requirements of processability and high T_g, a careful selection of diamines, such as rigid heterocyclic diamine 2-(4-aminophenyl)-5-aminobenzimidazole (BIA) and more flexible 4,4'-oxydianiline (ODA) are made. In order to obtain high performance melt processable PIs, end-capped co-PIs were prepared via one-step polycondensation using hydroquinone diphthalic anhydride (HQDPA) as an aromatic bridged dianhydride which has three isomers (Scheme 1) [8].



Scheme 1 PIs derived from HQDPA, BIA and ODA

The first series of PIs were synthesized from 3,3′-HQDPA with varying molar concentration of structurally different diamines while the second series of PIs were prepared by varying 3,3′-HQDPA and 4,4′-HQDPA molar ratio from 100 to 0% (Table 1). The typical thermal properties and melt complex viscosity of copolyimides are shown in Table 2, Fig. 1 and Fig. 2.

Table 1. Monomers molar ratio and inherent viscosity of copolyimides.

Polymer	Ratio of Diamines (%)		Ratio of Dianhydride (%)		PA	η_{inh}
	BIA	ODA	3,3′-HQDPA	4,4′-HQDPA	(%)	(dL/g)
PI-0a	100	0	100	0	5	0.47
PI-2a	98	2	100	0	6	0.48
PI-4a	96	4	100	0	6	0.47
PI-10a	90	10	100	0	6	0.50
PI-20a	80	20	100	0	6	0.44
PI-20b	80	20	75	25	6	0.47
PI-20c	80	20	50	50	6	0.49
PI-20d	80	20	25	75	6	0.47
PI-20e	80	20	0	100	6	-

Table 2. Thermal properties and melt complex viscosity of copolyimides.

PIs	T_g (°C)		$-d\log E'/dT$ [e]	MFI [a]	η*[pa·s] at	
	DSC	DMA			380 °C	400°C
PI-0a	360	354	_[b]	_[b]	-	-
PI-2a	-	346	1.5	1.5	-	2711
PI-4a	339	345	1.8	1.8	11262	3859
PI-10a	326	335	2.2	2.2	4112	1618
PI-20a	320	328	10.8	10.8	1517	379
PI-20b	312	330	7.8	7.8	2807	773
PI-20c	305	330	6	6	3478	1487
PI-20d	302	315	-	-	-	-
PI-20e	315	-	-	-	-	-

[a] Melt flow index measured at a load of 12.5 kg and a temperature of 380 °C. [b] Melt flow was not observed.

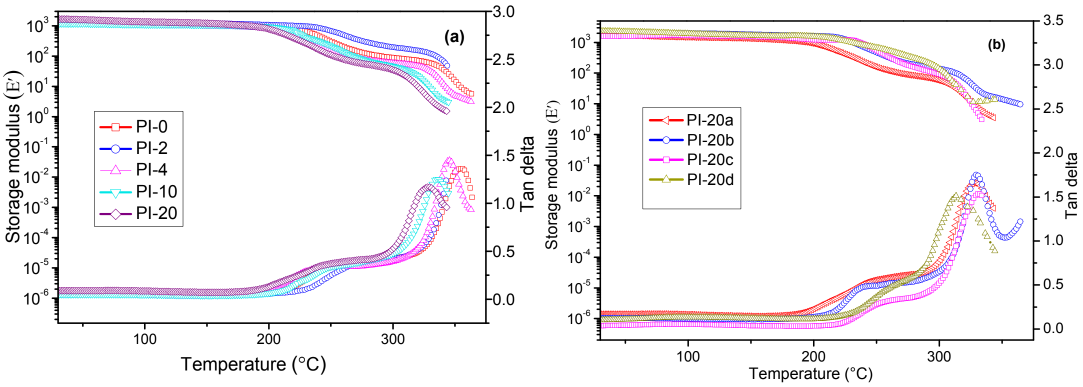


Fig. 1. Tan δ and dynamic storage modulus (E′) as a function of temperature of copolyimides

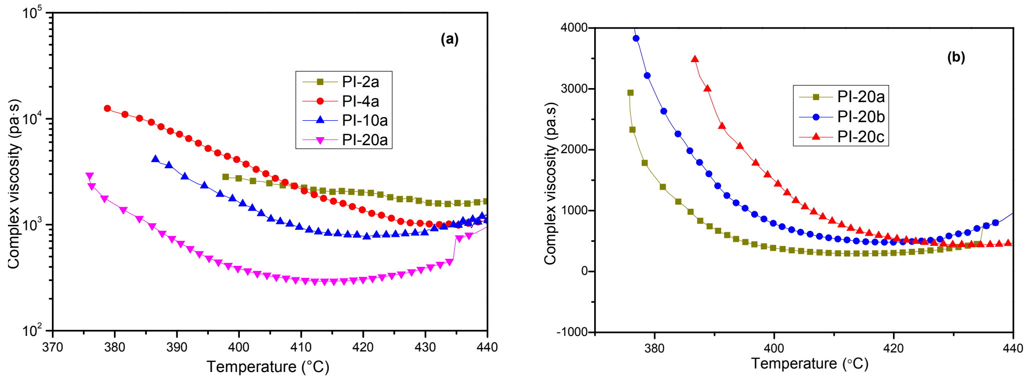
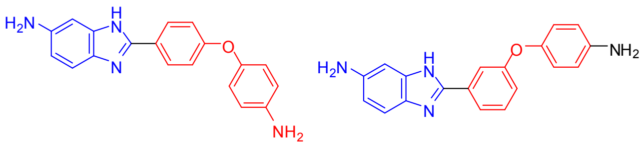


Fig. 2. Complex viscosity of copolyimides as a function of temperature.

Furthermore, with an aim to develop high performance and processable PIs, two novel unsymmetrical benzimidazole containing isomeric diamines, mimic of both BIA and ODA together were designed and prepared as depicted in Scheme 2, with an expectation to influence the chain flexibility of aromatic polyimides. Polymerization of diamine 1p with several dianhydrides was performed via conventional two-step method to afford the novel PI-4(a-e) series while one step polymerization was employed to get PI-5(c-e) series from 1m diamine (Table 3). Two new series of poly(benzimidazole imide)s (PBIPIs) were exhibited excellent thermal stability ($T_{5\%}$ = 503-559 °C), high T_g values (276-383 °C) and good mechanical properties (tensile strengths of 98-151 MPa and tensile moduli of 3.5-5.2 GPa). Controlled molecular weight (*Mw*) polymer derived from *meta* linkage demonstrated good solution and melt processability [9]. The typical thermal properties and melt complex viscosity of polyimides are shown in Table 4, Fig. 3 and Fig. 4.



1p 1m

Scheme 2 Novel BI-diamine structures.

Table 3. Inherent viscosity and film forming ability of polymers.

PBIPI	dianhydride	diamines	η_{inh}^{a} (dL/g)	η_{inh}^{b} (dL/g)
PBIPI -4a	BPDA	1p	0.41	-
PBIPI -4b	BTDA	1p	0.39	-
PBIPI -4c	ODPA	1p	0.42	-
PBIPI -4d	6FDA	1p	0.50	-
PBIPI -4e	BPADA	1p	0.48	-
PBIPI -5c	ODPA	1m	-	0.68
PBIPI -5d	6FDA	1m	-	0.50
PBIPI -5e	BPADA	1m	-	0.77
PBIPI -4e-PA	BPADA	1p	-	0.48
PBIPI -5e-PA	BPADA	1m	-	0.50

[a] Inherent viscosity of polyamic acid measured using 0.5 g/dL in NMP at 30 °C.
[b] Inherent viscosity of polyimide measured using 0.5 g/dL in NMP at 30 °C.

Table 4. Thermal properties of polymers.

PBIPIs	T_g (°C)		MFI[a]	η* [pa·s] at		
	DSC [a]	DMA [b]		350 °C	380 °C	400 °C
PBIPI -4a	383	385	-	-	-	-
PBIPI -4b	373	373	-	-	-	-
PBIPI -4c	346	358	-	-	-	-
PBIPI -4d	358	384	-	-	-	-
PBIPI -4e	282	287	-	-	-	-
PBIPI -5c	331	335	-	-	-	-
PBIPI -5d	347	359	-	-	-	-
PBIPI -5e	276	268	-	-	-	-
PBIPI -4e-PA	278	-	0.16 [b]	7048	6.2×10^3	7.1×10^3
PBIPI -5e-PA	263	-	6.67 [c]	-	2.6×10^3	2.3×10^3

[a] Melt flow index measured at a load of 12.5 kg/10 min at temperature of [b] 350 °C and [c] 360 °C .

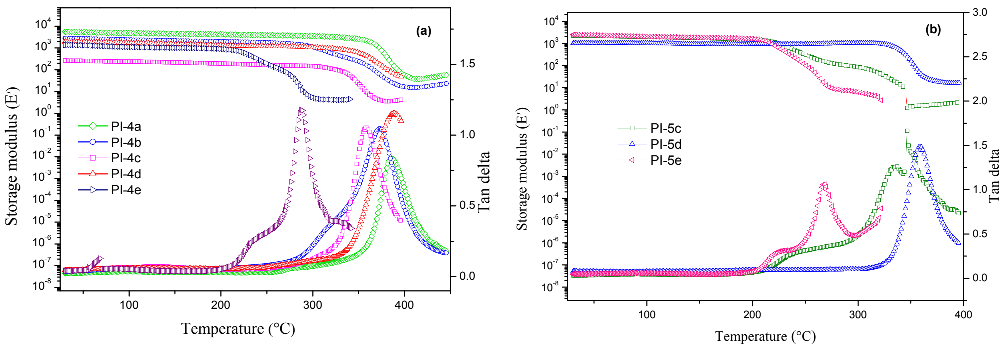


Fig 3. Tan δ and dynamic storage modulus (E′) as a function of temperature of PBIPIs

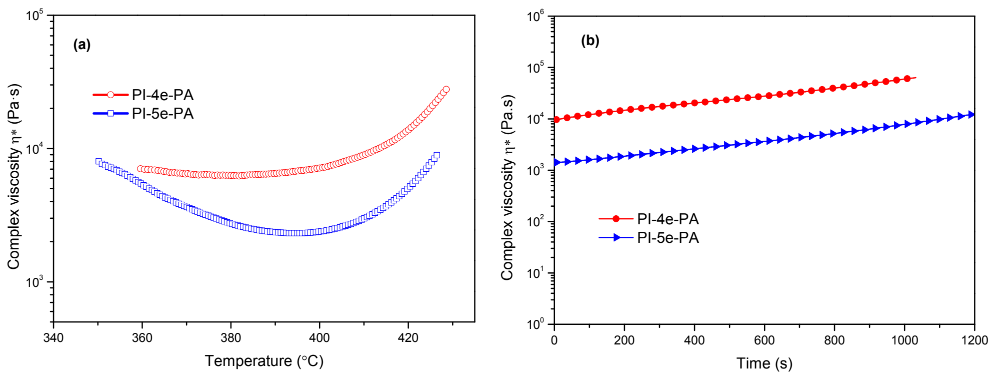


Fig 4. Complex viscosity of end-capped PIs as a function of (a) temperature (b) time.

References:

[1]M.K. Ghosh, K. L. Mittal (Eds.), Polyimides: Fundamentals and Applications;, Marcel Dekker, New York, 1996.(more references goto p6)