

Imide Oligomers Containing Novel Phenylethynyl-Pendent

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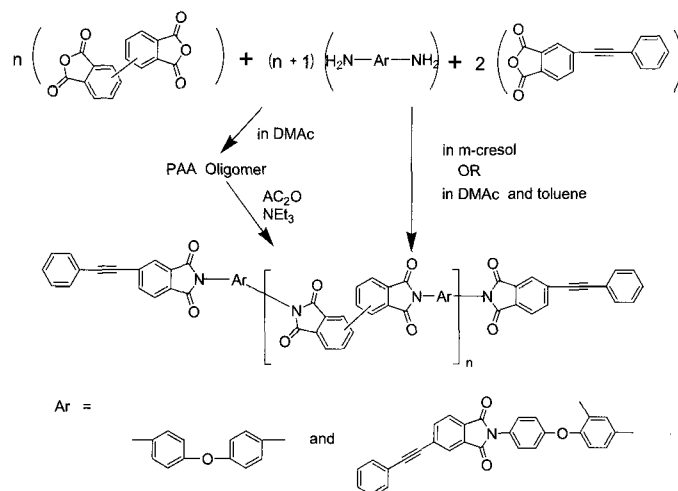
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Abstract: A novel pendent phenylethynyl-containing diamine, 2,4-Diamino[4'-(4-phenylethynylphthalimido)] diphenyl ether, was synthesized and imide oligomers containing pendent and terminal phenylethynyl groups were prepared from the reaction of isomeric biphenyltetracarboxylic dianhydride (3,3'-BPDA, 3,4'-BPDA and 4,4'-BPDA), 4,4'-oxydianiline (4,4'-ODA), 2,4-Diamino[4'-(4-phenylethynylphthalimido)] diphenyl ether and 4-phenylethynyl phthalic anhydride (4-PEPA) at an approximate number average molecular weight of 2500 and 5000 g mol⁻¹. The imide oligomers were characterized and thermally cured, and the thermal and mechanical properties of the cured polymers evaluated as thin films. The lower molecular weight oligomers exhibited higher cured glass transition temperature (T_g) and better melt processability without significantly sacrificing films tensile toughness. Imide oligomers with terminal phenylethynyl groups could be easily cast to flexible and tough films. Isomeric effect on polyimide properties were discussed and imide oligomers from 3,3'-BPDA and 3,4'-BPDA show good processability, moreover, 3,3'-BPDA based imide oligomers exhibited lower melt viscosity and cured resins possessed similar T_g with those from 3,4'-BPDA.



Scheme 1: Chemical structures of dianhydride isomers



Scheme 2: Preparation of imide oligomers containing pendent and terminal phenylethynyl group

Table 1: Composition of imide oligomers

Oligomer- n			Composition ^d	Calc. <i>M_n</i> (g/mol)
			BPDA/(4,4-ODA,DPEB)/PEPA = n/(n+1)/2	
Oligomer - 10	OI-1	3,3 ^{ra} -PEPTI-5000 ^b -20 ^c	10/(8.8,2.2)/2	5486.4
	OI-2	3,4'- PEPTI -5000-20		
	OI-3	4,4'- PEPTI -5000-20		
	OI-4	3,3'- PEPTI -5000-10	10/(9.9,1.1)/2	5363.2
	OI-5	3,4'- PEPTI -5000-10		
	OI-6	4,4'- PEPTI -5000-10		
Oligomer - 5	OI-7	3,3'- PEPTI -2500-20	14/(4,1)/2	2604
	OI-8	3,4'- PEPTI -2500-20		
	OI-9	4,4'- PEPTI -2500-20		
	OI-10	3,3'- PEPTI -2500-10	4/(4.5,0.5)/2	2548
	OI-11	3,4'- PEPTI -2500-10		
	OI-12	4,4'- PEPTI -2500-10		

a: "3,3" represents 3,3'-BPDA, "3,4" represents 3,4'-BPDA, "4,4" represents 4,4'-BPDA

b: Approximate number average molecular weight of imide oligomers

c: Mole concentration of pendent phenylethynyl-containing diamine in diamine monomers

d: Mole ratios of monomers

Table 2: Thermal and mechanical properties of unoriented thin films cured for 1h at 370°C in air

Oligomer		<i>T_g</i> /(°C)	Strength (MPa)	Modulus (GPa)	Elongation at break(%)
OI-1	3,3'-PTI-5000-20	357	98.7	1.1	15.3
OI-2	3,4'-PTI-5000-20	364	108.4	1.4	16.9
OI-3	4,4'-PTI-5000-20	—	120.8	1.9	15.8
OI-4	3,3'-PTI-5000-10	342	109.2	1.2	16.7
OI-5	3,4'-PTI-5000-10	350	112.2	1.4	19.2
OI-6	4,4'-PTI-5000-10	—	123.7	1.4	20.1
OI-7	3,3'-PTI-2500-20	364	124.5	1.4	19.3
OI-8	3,4'-PTI-2500-20	364	102	1.4	14.5
OI-9	4,4'-PTI-2500-20	—	120.5	1.4	19.8
OI-10	3,3'-PTI-2500-10	354	113.6	1.2	19.7
OI-11	3,4'-PTI-2500-10	361	102	1.4	17.8
OI-12	4,4'-PTI-2500-10	—	121	1.5	19.2

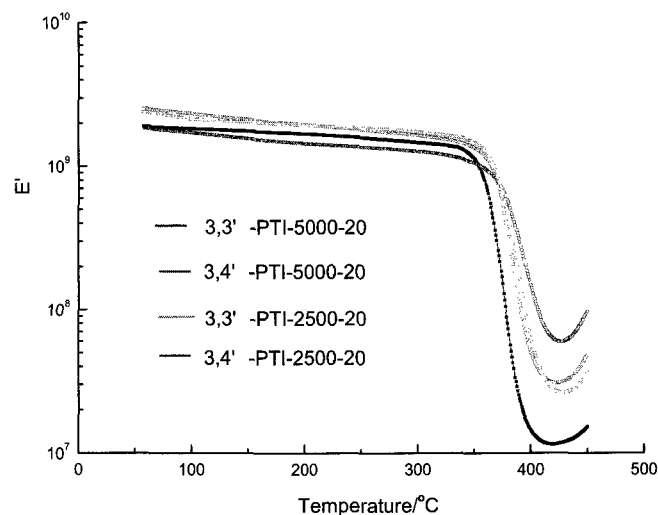


Figure 1: Temperature dependence of dynamic tensile properties (DMA curves) of OI-1, OI-2, OI-7 and OI-8

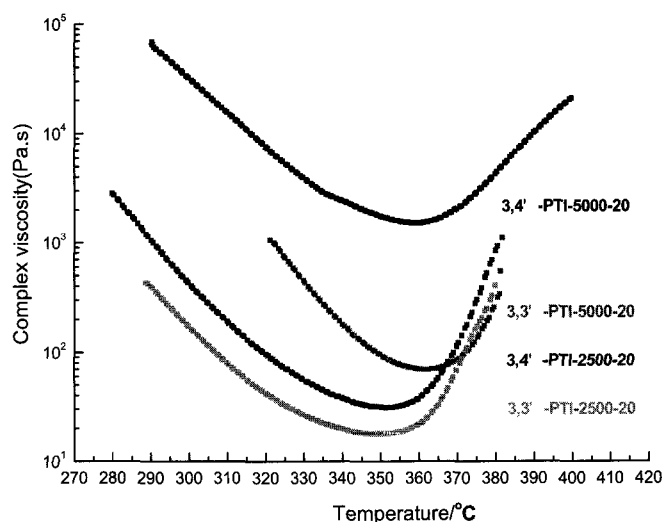


Figure 2: The rheological behavior of OI-1, OI-2, OI-7 and OI-8

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