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Fluorinated phenylethynyl-terminated imide oligomers with reduced melt viscosity and enhanced melt stability

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ABSTRACT

Two novel fluorinated phenyethynyl-contained endcapping agents, 4-(3-trifluoromethyl-1-phenylethynyl)phthalic anhydride (3F-PEPA) and 4-(3,5-bistrifluoromethyl-1-phenylethynyl)phthalic anhydride (6F-PEPA) were synthesized, which were employed to synthesize two fluorinated model compounds, Nphenyl-4(3-trifluoromethyl)-phenylethynylphthalimide (3F-M) and N-phenyl-4(3,5-bitrifluoromethyl)phenylethynyl phthalimide (6F-M). The thermal cure kinetics of 3F-M and 6F-M were analyzed using DSC and compared to the unfluorinated derivative, N-phenyl-4-phenylethynylphthalimide (PEPA-M). The thermal cure temperatures of 3F-M and 6F-M were 399 and 412 °C, which were 22 and 35 °C higher than that of PEPA-M, respectively. The thermal cure kinetics of 3F-M and 6F-M best fit a first-order rate law, although 3F-M and 6F-M reacted slower than PEPA-M. However, the exothermic enthalpy of 3F-M and 6F-M were only half of PEPA-M. Based on the model compounds study, a series of fluorinated phenylethynyl-terminated imide oligomers (F-PETIs) with different calculated molecular weights (Calc'd $M_{\rm n}$) were synthesized by thermal polycondensation of 2,3,3',4'-biphenyltetracarboxylic acid dianhydride (a-BPDA) and 3,4'-oxydianiline (3,4'-ODA) using 3F-PEPA or 6F-PEPA as the endcapping agent. The substituent effects of the trifluoromethyl (-CF₃) groups on the thermal cure behavior and melt processability of F-PETIs were systematically investigated. Experimental results reveal that the melt processability of F-PETI was apparently improved by the reduced resin melt viscosities and the enhanced melt stability due to the incorporation of the $-CF_3$ groups in the imide backbone. All of those F-PETIs exhibit outstanding thermal and mechanical properties.

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1. Introduction

In recent years, significant efforts have been attempted in improving the melt processability of aromatic polyimides [1–8]. Introduction of phenylethynyl-endcapping groups into the low-molecular-weight imide oligomers was confirmed to be an effective approach [9,10]. Phenylethynyl-terminated imide oligomers (PETIs), due to its good melt processability and the great combination of thermal and mechanical properties etc., have been extensively employed as the matrices of carbon fiber-reinforced polyimide composites for high temperature applications [11–33]. Compared with nadic- or maleic-endcapped resins, phenylethynyl-endcapped imides could be thermally cured by much preferred chain extension than crosslinking, affording thermoset resins with better impact strength [34–36].

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The polyimide composites derived from PETI could be produced either by autoclave [11–27] or by resin transfer molding (RTM) [28–33], resulting in composite materials with high strength and modulus as well as excellent thermal stability. PETI-5, the representative PETI with Calc'd M_n of 5000 g/mol could be melt processed by autoclave at 360–370 °C [16,18]. By reducing Calc'd M_n of PETI-5 to 1000 g/mol, imide oligomers with much lower melt viscosity and suitable for RTM have been successfully developed. The representative RTM imide resins (such as PETI-298, PETI-330 and PETI-375) could be melt at 260-280 °C and completed the thermal curing at 360-370 °C [29,30,32,33]. In the case of RTM application, the melt processability of PETI was endorsed by its low molecular weights as well as its flexible chemical backbone. However, the very low molecular weights of PETI usually result in the thermal-cured materials with poor impact toughness and the flexible oligomer backbone leads to the low glass transition temperatures (T_g) for the thermal-cured resins. Hence, to improve the RTM processability of PETI by reducing the melt viscosity and enhancing the melt stability is still of great concern to high temperature polyimide composites. Moreover, many other efforts





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have been made to improve the RTM melt processability of PETI such as (1) by introducing comonomers for copolycondensation; (2) by mixing of low-viscous reactive diluents, or (3) by introducing asymmetric aromatic structures into the resin chemical backbone etc. [29-31,37-39].

Meanwhile, it was also found that by replacing the phenylethynyl-endcapping groups in the imide oligomers with naphthyl or anthracenyl-endcapping groups could decrease the cure temperature by 30–80 °C and accelerate the thermal cure reaction [40–43]. It was reported that the imide oligomers endcapped with 4-(2-phenylethynyl)-1,8-naphthalic anhydride (PENA), or 4-(1-naphethlethynyl)-1,8-naphthalic anhydride (NENA) cure at faster rate at a temperature nearly 30 °C lower [44], attributed by the electronwithdrawing effects of the multi-aromatic structures on the electron density and distribution of the ethynyl group in the imide oligomers. Researchers also noted that imide oligomers derived from 4-phenylethynyl phthalic anhydride (4-PEPA) with different substituted groups and 3-phenylethynyl phthalic anhydride (3-PEPA) exhibit different thermal curing behaviors [21,45].

Usually the endcapping agent could affect the properties of the imide oligomers and their final cured polyimides profoundly for the extra-high density of endcapping groups in imide oligomers. Although many researchers have designed novel endcapping agents to develop new imide resins, few studies on the imide oligomers derived from fluorinated phenyethynyl-contained endcapping agents could be found in the literature. In efforts to enhance the melt processability (including the melt viscosity and melt stability) of imide oligomers with high molecular weights, it is reasoned that introduction of the bulky trifluoromethyl in phenylethynyl-endcapping group to lower the interchain interaction or reduce the stiffness of polymer backbone, this should make it possible to maintain higher-molecular weights for oligomers to enhance the mechanical/thermal properties for their corresponding thermalcured resins. Meanwhile fluoro-containing substituents with outstanding thermal stability could also affect the properties of the cured polyimide.

In the present research, two novel fluorinated phenyethynylcontained endcapping agents were synthesized. The work reported herein was performed primarily to determine whether substituting fluorinated groups (e.g. –CF₃) in the phenylethynyl group of PEPA offered any distinct advantages in the physical and/or thermal cure properties and also to determine the melt processability, the thermal curing and mechanical properties of the fluorinated PETI and their thermal-cured polyimides.

2. Experimental

2.1. Materials

2.3'.3.4'-biphenvltetracarboxylic acid dianhydride (*a*-BPDA, mp: 196–197 °C) and 4-phenylethynyl phthalic anhydride (4-PEPA, mp: 151–152 °C) were synthesized in this laboratory according to the reported methods [46,47]. 3,4'-oxydianiline (3,4'-ODA, mp: 84-85 °C) was purchased from Shanghai Baicheng Chemicals Corp., China and recrystallized from ethanol/water (1:1) prior to use. 4-bromophthalic anhydride was purchased from Beijing Bomi Chemicals Corp., China and recrystallized from acetic acid/acetic anhydride prior to use. N-methyl-2-pyrrolidinone (NMP) was purchased from Beijing Beihua Fine Chemicals, China and purified by vacuum distillation over P2O5. Triethylamine was used after vacuum distillation in the presence of calcium hydride. 1-bromo-3-(trifluoromethyl)benzene and 1-bromo-3,5-bis(trifluoromethyl) benzene were purchased from Liaoning Fuxin Sanbao Chemicals Corp., China and used as received. 2-methyl-3-butyn-2ol was purchased from Beijing Beihua Hengyuan Chemicals Corp., China and used as received. All other reagents were commercially obtained from China National Medicines Corp., China and used as received.

2.2. Measurements

Infrared spectra (IR) were measured on a Perkin–Elmer 782 Fourier transform infrared (FTIR) spectrometer. ¹H and ¹³C NMR spectra were obtained on a Bruker AVANCE 400 spectrometer at frequencies of 400 MHz using chloroform-d or DMSO- d_6 as solvents. Differential scanning calorimetry (DSC) analysis was performed on a TA-Q100 analyzer at a heating rate of 10 °C/min in nitrogen atmosphere. Thermogravimetric analysis (TGA) was accomplished on a TA-Q50 series thermal analysis system at a heating rate of 20 °C/min in nitrogen atmosphere. Complex viscosity was performed on a TA-AR 2000 rheometer using the test specimen disks with diameter of 25 mm and thickness of 1.2 mm, which were prepared by compression molding of the imide oligomer powders at room temperature. The test disks were loaded in the rheometer fixture equipped with 25 mm diameter parallel plates, in which the top plate was oscillated at a fixed strain of 5% and a fixed angular frequency of 10 rad/s whereas the lower plate was attached to a transducer for detecting the resultant torque. For the tests of dynamic thermal melt complex viscosity, the test specimens were scanned from 200 °C at a heating rate of 4 °C/min, in which the melt viscosity (η^* , complex viscosity as a function of time) was determined. Gel permeation chromatography (GPC) was performed on Waters system that was equipped with a model 1515 pump, a 2414 refractive index detector using NMP as the eluant at a flowing rate of 1.0 ml/min. The sample concentration was 1 mmol/ml and monodisperse polystyrene was employed as the standard sample. Matrix-assisted laser desorption/ionization timeof-flight (MALDI-TOF) mass spectra were carried out with a Biflex IIIMALDI-TOF mass spectrometer (Bruker, Billerica, Germany) equipped with delayed extraction, a multisample probe, a time-offlight reflection analyzer, a nitrogen laser with a wavelength of 337 nm and a pulse width of 3 ns, and a linear flight path length of 100 cm, in which the flight tube was evacuated to 1027 Pa. Mechanical properties were obtained with an Instron model 3365 universal tester at room temperature. The tensile strength, modulus, and the elongation at breakage were measured in accordance with GB/T 16421-1996 at a strain rate of 2 mm/min.

2.3. Synthesis of 3-trifluoromethyl-1-ethynylbenzene (3F-EB)

1-bromo-3-(trifluoromethyl)benzene (22.50 g, 0.1 mol), 2-methyl-3-butyn-2-ol (10.09 g, 0.12 mol), cuprous iodide (0.95 g, 5 mmol), triphenylphosphine (0.65 g, 2.5 mmol), bis (triphenylphosphine)palladium dichloride (1.40 g, 2.0 mmol) and triethylamine (200 ml) were added into a 500 ml three-necked flask equipped with a water condenser, a mechanical stirrer and nitrogen inlet/outlet. The reaction mixture was heated to reflux for 8 h, and cooled to room temperature. The catalyst and produced salt were separated by filtration to give a filtrate, which was then performed on a rotary evaporator to remove the solvent and yield a white solid. The crude product was washed twice with hot water and transferred into a 250 ml flask equipped with Dean-Stark trap containing 100 ml cyclohexane and sodium hydroxide (0.50 g, 12.5 mmol). The resulting solution was heated to reflux for 2 h and then hot filtrated. After cooled to ambient temperature, the filtrate was vacuum distillated (5 mmHg) to give a colorless liquid with boiling point of 87-88 °C (11.74 g, yield: 69.0%). ¹H NMR (chloroform-d, δ ppm): 7.65 (s, 1H), 7.55–7.50 (t, 2H), 7.41–7.36 (t, 1H), 2.57 (s, 1H). Anal. calcd for C₉H₅F₃: C, 63.54%; H, 2.96%. Found: C, 63.57%; H, 2.93%.

2.4. Synthesis of 3,5-bitrifluoromethyl-1-ethynylbenzene (6F-EB)

This intermediate compound was obtained by the similar method as described above except that 1-bromo-3-(trifluoromethyl)benzene was replaced by 1-bromo-3,5-(bitrifluoromethyl)benzene. The product was colorless liquid with boiling point of 61–62 °C (15.24 g, yield: 64.0%). ¹H NMR (chloroform-*d*, δ ppm): 7.91 (s, 2H), 7.84 (s, 1H), 3.25 (s, 1H). Anal. calcd for C₁₀H₄F₆: C, 50.44%; H, 1.69%. Found: C, 50.47%; H, 1.72%.

2.5. Synthesis of 4-(3-trifluoromethyl-1-phenylethynyl)phthalic anhydride (3F-PEPA)

A mixture of 4-bromophthalic anhydride (22.70 g, 0.10 mol), 3F-EB (18.70 g, 0.11 mol) and triethylamine (250 ml) were added into a 500 ml flask equipped with a mechanical stirrer, a water condenser and a nitrogen inlet. The reaction mixture was stirred at room temperature until a homogeneous solution was obtained. Cuprous iodide (0.95 g, 5.0 mmol), triphenylphosphine (0.66 g, 2.5 mmol), bis (triphenylphosphine)palladium dichloride (1.40 g, 2.0 mmol) were then added. After refluxed under nitrogen atmosphere for 6 h, the reaction mixture was cooled to room temperature and then filtrated to remove the catalyst and salt generated in the reaction. The filtrate was poured into 800 ml of water, and then acidified to pH = 2 with concentrated hydrochloric acid (35–38%). The precipitate was collected and vacuum dried at 120 °C for 5 h to give a yellow powder. The obtained solid was dissolved in 200 ml of toluene in a 500 ml flask equipped with mechanical stirrer, a water condenser, a Dean–Stark trap and a nitrogen inlet. The solution was heated to reflux for 8 h under nitrogen atmosphere, in which the water generated in the reaction was simultaneously removed by azeotropic distillation. And the solution was then concentrated by partly removal of toluene. The concentrated solution was cooled to room temperature and yielded yellow solid. After filtrated and rinsed with acetic acid, the crude product was purified by recrystallization in acetic acid/acetic anhydride (2:1 v/v) to afford 23.10 g of yellow crystal (yield: 73.0%). mp: 162–163 °C [determined by DSC]. ¹H NMR (chloroform-*d*, δ ppm): 8.14 (s, 1H), 8.01 (s, 2H), 7.84 (s, 1H), 7.76–7.74 (d, 1H), 7.69–7.67 (d, 1H), 7.57–7.53 (t, 1H). ¹³C NMR (chloroform-*d*, δ ppm): 162.9, 139.3, 136.0, 132.7, 131.4, 131.3, 131.1, 131.0, 129.1, 129.0, 128.5, 126.7, 126.6, 125.8, 123.6, 123.1121.3, 93.2, and 89.0. FTIR (KBr cm⁻¹): 2207 (−C≡C−), 1840 (asym C=O str), 1782 (sym C=O str), 1146 (C-F). Anal. calcd for C₁₈H₆F₆O₃: C, 64.57%; H, 2.23%. Found: C, 64.36%; H, 2.08%.

2.6. Synthesis of 4-(3,5-bistrifluoromethyl-1-phenylethynyl) phthalic anhydride (6F-PEPA)

6F-PEPA (yellow crystal, 26.88 g, yield: 70.0%) was obtained by the similar method as described above except that 3F-EB was replaced by 6F-EB. mp: 196–197 °C ¹H NMR (DMSO-*d*₆, δ ppm): 8.41 (s, 1H), 8.35 (s, 1H), 8.25 (s, 1H), 8.17 (s, 2H), 3.32 (s, 1H). ¹³C NMR (chloroform-*d*, δ ppm): 162.9, 139.5, 133.0, 132.8, 132.7, 132.3, 132.0, 131.9, 130.4, 128.8, 127.8, 126.4, 125.3, 125.1, 123.5, 122.4, 119.5, 93.2, and 89.0. FTIR (KBr cm⁻¹): 2187 (–C≡C–), 1837 (asym C=O str), 1795 (sym C=O str), 1136 (C–F). Anal. calcd for C₁₇H₇F₃O₃: C, 56.27%; H, 1.57%. Found: C, 56.10%; H, 1.65%.

2.7. Synthesis of model compounds

Model compounds including N-phenyl-4-(3-trifluoromethyl-1-phenylethynyl)phthalimide (3F-M), N-phenyl-4-(3,5-bitrifluoromethyl-1-phenylethynyl)phthalimide (6F-M) and N-phenyl-4-(1phenylethynyl)phthalimide (PEPA-M) were prepared by chemical cyclodehydration. In a typical experiment, 3F-M was prepared in the following procedure: 4-(3-trifluoromethyl-1-phenylethynyl) phthalic anhydride (31.60 g, 0.1 mol), aniline (9.31 g, 0.1 mol) and 150 ml DMAc were placed in a 500 ml flask equipped with a water condenser and a mechanical stirrer. The reaction solution was stirred at room temperature for 4 h. The solution was then chemically cyclodehydrated with acetic anhydride and pyridine (2:1 v/v)after stirring for 6 h. The resultant mixture was then poured into 300 ml of ethanol to vield precipitate. The solid was collected by filtration, and then dried at 100 °C in vacuum for 5 h to afford an off-white solid (36.50 g, yield: 93.3%). mp: 240–241 °C ¹H NMR (chloroform-d, δ ppm): 8.10 (s, 1H), 7.97–7.91 (m, 2H), 7.84 (s, 1H), 7.75-7.74 (d, 1H), 7.66-7.65 (d, 1H), 7.55-7.50 (m, 3H), 7.46-7.40 (m, 3H). FTIR (KBr cm⁻¹): 2205 ($-C \equiv C_{-}$), 1843 (asym C $\equiv O$ str), 1811 (sym C=O str), 1383 (imide C-N str), 1141 (C-F). Anal. calcd for C₂₃H₁₂F₃NO₂: C, 70.59%; H, 3.09%, N 3.58%. Found: C, 70.42%; H, 3.15%; N, 3.44%.

The model compound 6F-M was prepared according to above method except that 3F-PEPA was replaced with 6F-PEPA to afford off-white solid (43.51 g, yield: 94.7%). mp: 240–241 °C by DSC. ¹H NMR (chloroform-*d*, δ ppm): 8.12 (s, 1H), 8.01 (s, 2H), 8.00–7.93 (m, 2H), 7.89 (s, 1H), 7.54–7.50 (m, 2H), 7.45–7.41 (m, 3H). FTIR (KBr cm⁻¹): 2117 (–C=C–), 1853 (asym C=O str), 1820 (sym C=O str), 1392 (imide C–N str), 1147 (C–F). Anal. calcd for C₂₄H₁₁F₆NO₂: C, 62.75%; H, 2.41%; N 3.05%. Found: C, 62.77%; H, 2.42%; N, 3.05%.

The model compound PEPA-M as a comparative was prepared according to the method as described above except that 3F-PEPA was replaced with 4-PEPA to afford off-white solid (30.98 g, yield: 95.8%). mp: 203–204 °C. ¹H NMR (chloroform-*d*, δ ppm): 8.12 (s, 1H), 8.01 (s, 2H), 8.00–7.93 (m, 2H), 7.89 (s, 1H), 7.54–7.50 (m, 2H), 7.45–7.41 (m, 3H). FTIR (KBr cm⁻¹): 2117 (–C=C–), 1853 (asym C=O str), 1820 (sym C=O str), 1392 (imide C–N str), 1147 (C–F). Anal. calcd for C₂₄H₁₁F₆NO₂: C, 81.72%; H, 4.05%; N 4.33%. Found: C, 81.84%; H, 4.13%; N, 4.21%.

2.8. Synthesis of the fluorinated imide oligomers (F-PETIs)

F-PETIs were prepared by the conventional two-stage polymerization and imidization process. In a typical experiment, 3,4'-ODA (10.01g, 0.050 mol) and NMP (60 ml) were placed in a flask equipped with a water condenser, a mechanical stirrer, a Dean-Stark trap, a thermometer and a nitrogen inlet/outlet. After stirred for 30 min at room temperature to give a homogeneous solution, a slurry of a-BPDA (7.35 g, 0.025 mol), 3F-PEPA (15.81 g, 0.050 mol) and NMP (51 ml) was added. The reaction mixture, with 30% of solids (w/w), was stirred at 80 °C for 8 h and 150 ml toluene was then added. The resultant solution was heated to reflux at 185 °C for 10 h, in which the water evolved in the thermal imidization was simultaneously removed from the reaction system by azeotropic distillation. After cooled down to about 120 °C, the hot solution was poured slowly into 1000 ml of water. The solid was collected by filtration and washed with hot water three times, and then dried at 205 °C in vacuum for 10 h to give O1-1 as yellow powder (30.28 g, 96.6%).

Other F-PETIs including O1-2, O2-1, O2-2, O10-1, O10-2 as well as the unfluorinated derivatives including O1-*comp*, O2-*comp* and

Table 1	
Thermal data and kinetic	parameters of the model compounds.

		•				1		
Sample	Endothermal temperature (°C)	Exothermal temperature (°C)		ΔH (J/g)	E (kJ/mol)	n	Α	
	Peak	Onset	Peak	End				
PEPA-M 3F-M 6F-M	202 240 241	320 343 350	377 399 412	434 432 -	516 270 218	152.9 168.9 187.4	0.94 1.05 1.09	$\begin{array}{c} 8.1 \times 10^{11} \\ 5.0 \times 10^{12} \\ 8.2 \times 10^{11} \end{array}$

Table 2			
Chemical compositions and molecular	weights of F-PE	ΓIs and the	unfluorinated
derivatives.			

Sample	Chemical composition ^a	Calc'd Pn ^b	Calc'd M _n (g/mol) ^c	M _n (g/mol)	M _w (g/mol)	M_w/M_n
01–1	3,4'-ODA/a-BPDA/ 3F-PEPA = 2/1/2	1	1254	2555	4957	1.94
01–2	3,4'-ODA/a-BPDA/ 6F-PEPA = 2/1/2	1	1392	2854	4881	1.71
01–comp	3,4'-ODA/a-BPDA/ 4-PEPA = 2/1/2	1	1118	2253	5691	2.52
02–1	3,4'-ODA/a-BPDA/ 3F-PEPA = 3/2/2	2	1712	3410	5564	1.63
02–2	3,4'-ODA/a-BPDA/	2	1850	3521	8373	2.37
O2-comp	3,4'-ODA/a-BPDA/	2	1576	3248	4661	1.49
010-1	3,4'-ODA/a-BPDA/	10	5376	8197	16,172	1.97
010-2	3,4'-ODA/a-BPDA/	10	5514	10,826	20,943	1.93
O10-comp	3,4'-ODA/a-BPDA/ 4-PEPA = 11/10/2	10	5238	10,027	22,947	2.29

^a Molar ratios of the reactants.

^b Calculated polymerization degree.

^c Calculated molecular weight.

O10-*comp* were prepared according to the similar procedure, in which the molar ratios of 3,4'-ODA, *a*-BPDA and 3F-PEPA, 6F-PEPA, or 4-PEPA were listed in Table 2.

2.9. Preparation of the thermal-cured polyimides

The imide oligomer resin powders were placed in a die, which was then placed in a hot press preheated at 200 °C. The die temperature was increased gradually to 370 °C at a rate of 4 °C/min. After it was kept there for 10–25 min, the die was applied with a pressure of 1.0–3.5 MPa. After it was kept for 1h at 370 °C, the die was then cooled with the applied pressure to less than 200 °C. The thermally cured polyimide sheet was removed from the die at room temperature and then cut to the desired sizes for thermal and mechanical testing.

3. Results and discussion

3.1. Monomers

3F-EB and 6F-EB were successfully synthesized *via* a two-step procedure of coupling and cleavage reaction in the total yield of



Fig. 1. DSC curves of the model compounds at 20 °C/min.

69.0% and 64.0%, respectively. The first step was the coupling reaction of 2-methyl-3-butyn-2-ol with 1-bromo-3-(trifluoro methyl) benzene or 1-bromo-3,5-(bitrifluoromethyl)benzene in the presence of palladium catalyst to yield the intermediates 1-(2-methyl-3-butyn-2-ol)-3-(trifluoromethyl)benzene or 1-(2-methyl-3 -butyn-2-ol)-3,5-(bistrifluoromethyl)benzene, which was then treated with NaOH to give the intermediate compounds. 3F-PEPA and 6F-PEPA were prepared *via* the palladium-catalyzed coupling reaction of 4-bromophthalic anhydride with 3F-EB or 6F-EB as showed in Scheme 1. The resultant products were recrystallized in acetic acid/acetic anhydride (2:1 v/v) in the total yield of 73.0% and 70.0%, respectively. The molecular structures of 3F-PEPA and 6F-PEPA were confirmed by means of FTIR, ¹H and ¹³C NMR and elemental analysis.

3.2. Thermal curing properties of model compounds

Prior to imide oligomers and the thermal-cured polyimide studies, model compounds (3F-M, 6F-M and PEPA-M) were synthesized by the chemical cyclodehydration in good yield and characterized. The thermal behaviors of the model compounds were investigated by DSC to determine the effect of the molecular structures on their thermal curing behaviors. Fig. 1 shows the DSC curves of the model compounds (3F-M and 6F-M) compared with PEPA-M and Table 1 lists the DSC data. The sharp endothermic peaks in the range of 202–241 °C were assigned as the melt points





Fig. 2. Curing kinetic analysis and calculation of the thermal curing activation energy of the model compounds.

 $(T_{\rm m}{\rm s})$ and the wide exothermic peaks in the range of 377–412 °C were attributed to the thermal curing reactions of the phenyl-ethynyl groups in the model compounds.

The $-CF_3$ groups had pronounced impacts on the T_m s values and the thermal curing reaction of the phenylethynyl groups. The fluorinated model compounds (3F-M and 6F-M) showed the identical melting points (240 and 241 °C), 38–39 °C higher than PEPA-M (202 °C). 3F-M and 6F-M had the onset temperatures (343 and 350 °C, respectively), 23–30 °C higher than PEPA-M (320 °C). Meanwhile, the exothermal peak temperatures of 3F-M and 6F-M were 399 °C and 412 °C, respectively, 22–35 °C higher than PEPA-M (377 °C), indicating that the fluorinated phenylethynyl groups would undergo thermal curing at higher temperatures than the unfluorinated analogue. In comparing the reaction exothermal data, 3F-M ($\Delta H = 270$ J/g) and 6F-M ($\Delta H = 218$ J/g) had much lower exothermic enthalpies than PEPA-M ($\Delta H = 516$ J/g), implying that the fluorinated phenyethynyl group would undergo the thermal curing with much lower exotherm.

In order to extensively understand the thermal curing reaction of the phenylethynyl-endcapped imide oligomers, the nonisothermal



Fig. 3. Representative GPC curves of F-PETIs with different Calc'd M_n.

DSC method was employed to study the curing kinetics of the model compounds and the resultant data are also tabulated in Table 1. In the experiments, temperatures of the model compounds (3F-M, 6F-M and PEPA-M) were scanned by DSC at different heating rates (2, 5, 10, 15 and 20 °C/min, respectively). The exothermic peak temperatures (T_p) in DSC curves were shifted into higher temperatures with increasing of the heating rate (β). Kissinger's method is based on the fact that T_p varies with β and assumes that the maximum reaction rate ($d\alpha/dt$) occurs at peak temperatures [48]. Thus, the equation can be expressed as follows (Equation (1)):

$$-\ln(\beta/T_{\rm p}^2) = \ln(E/R) - \ln(An) - (n-1)\ln(1-x)_{\rm p} + E/RT_p$$
(1)

where *E* is the activation energy; *R* is the gas constant; *A*, *n* and *x* are the pre-exponential factor, the order of the cure action, and the extent of the cure action, respectively. Fig. 2 shows the scatter graphs of $-\ln(\beta/T_p^2)$ against $1/T_p$. The calculated values of *E*s for PEPA-M, 3F-M and 6F-M were 152.9, 168.9, and 187.4 kJ/mol, respectively.



Cured imide oligomers

Scheme 2. Synthesis of F-PETIs and the thermal-cured polyimides.



Fig. 4. MOLDI-TOF mass spectra of F-PETIs with different Calc'd $M_{\rm n}$.

Obviously, 3F-M and 6F-M, the fluorinated phenylethynyl-endcapped imide compounds, have higher *Es* than PEPA-M. Meanwhile, 6F-M, with two $-CF_3$ groups in the phenylethynyl group, has higher *E* value (187.4 kJ/mol) than 3F-M (168.9 kJ/mol). This could be interpreted by the stronger electron-withdrawing effect and steric hindrance of the $-CF_3$ in the phenylethynyl group. If the *E* value was introduced into the Crane's equation (2):

$$d(\ln\beta)/d(1/T_p) \approx -E/nR \tag{2}$$

The scatter plot of $\ln(\beta)$ as a function of $1/T_p$ can be obtained as shown in Fig. 2, in which the *n* values were obtained as 0.94 for PEPA-M, 1.05 for 3F-M, and 1.09 for 6F-M, respectively, demonstrating that the thermal curing reaction of the model compounds fit the first-order kinetics reaction rate law, similar to other electron-

Table 3 Molecular structures of the chemical species detected by MOLDI-TOF mass spectra for F-PETIs with different Calc'd M_n

	Chemical structures of the resin species	п	Mass (<i>m/z</i>)	Intensity %
		0	819.7	1.5
	PEPA-M	1	1277.4	100.0
	Endo	2	1735.4	84.7
		3	2193.4	62.2
	AT Same and a second	4	2651.5	25.5
	J J J J J J J J J J J J J J J J J J J	5	3110.7	6.1
01-1	Exo			
	GF-M			
	or and a set			
	190 200 200 300 400 400 Temperature (°C)			
	F_3C () R_3^+	0	819.4	3.6
		1	1277.4	87.8
		2	1735.4	100.0
01.2	CF3	3	2193.4	92.9
01-2	o (o o) n	4	2652.4	29.6
	double-endranning species	5	3110.6	2.0
		1	1277.4	16.3
		2	1735.4	69.4
		3	2194.4	100.0
		4	2652.4	84.7
		5	3110.5	54.1
		6	3569.0	33.7
	double-endcapping species	7	4029.1	20.4
		8	4487.6	8.2
		9	4947.2	4.1
01-10	/ 0\ 0 - Na ⁺	1	1021.5	32.7
		2	1479.5	62.2
		3	1937.4	86.7
		4	2396.4	61.2
	\ ~ 0 ^{//} 1/ 0 [/] /n'	5	2854.5	31.6
		6	3312.7	15.3
	mana andeanning aperica	7	3771.1	7.1
	mono-enacapping species			

withdrawing arylethynyl-endcapped imide oligomers [40–43]. Moreover, the pre-exponential factors (*A*) in the range of 8.2×10^{11} to 5.0×10^{12} for the fluorinated model compounds could also be obtained according to the Kissinger's equation as shown in Table 1.

Besides the electronic effects, the trifluoromethyl group might have some steric hindrance to retard the thermal curing reaction of



Fig. 5. DSC curves of the representative F-PETIs with different Calc'd Pn.

the phenylethynyl group, which resulted in the elevated thermal curing temperatures.

3.3. Molecular structures of F-PETIs

A series of F-PETIs with various Calc'd P_n (calculated polymerization degree) and different endcapping agents including 3F-PEPA, 6F-PEPA or 4-PEPA were prepared by the synthetic pathway as shown in Scheme 2 and their chemical compositions are summarized in Table 2.

The stoichiometric compositions of the monomers including aromatic dianhydride (i.e. α -BPDA) and aromatic diamine (i.e. 3,4'-ODA) and the endcapping agents were changed systematically in order to explore the influence of the oligomer molecular weights

Table 4	
Thermal curing behaviors of F-PETIs with	h different Calc'd M_n determined by DSC.

Sample	$T_{\rm g}(^{\circ}{\rm C})$	T_{onset} (°C)	$T_{\rm exo}$ (°C)	⊿H (J/g)
01-1	136	312	406	192.6
01-2	143	325	421	174.7
O1-comp	137	293	397	240.1
02-1	165	323	413	139.1
02-2	170	334	424	109.6
O2-comp	168	315	392	178.5
010-1	229	388	435	7.81
010-2	217	398	441	5.67
O10-comp	218	379	422	9.64



Fig. 6. Dynamic rheological behaviors of representative F-PETIs with different Calc'd $M_{\rm p}$.

and $-CF_3$ groups on the imide oligomer properties. The Calc'd P_n of the imide oligomers were designed to be 1, 2 and 10, respectively, by controlling the molar ratios of *a*-BPDA to 3,4'-ODA along with the endcapping agents including 3F-PEPA, 6F-PEPA or 4-PEPA (Table 2), resulting in a series of F-PETIs with different Calc'd M_n in the range of 1254–5514 g/mol.

Table 2 also shows the molecular weights of the synthesized imide oligomers determined by GPC using NMP as solvent, including the number average molecular weight (M_n), weight average molecular weight (M_w), and the molecular weight distribution (M_w/M_n). The measured molecular weights are much higher than the calculated ones due to the polarity difference of the testing samples compared to the GPC standard sample (polystyrene) [30]. For instance, O1-1 has the measured M_n of 2555 g/mol, almost doubled the Calc'd M_n (1254). The molecular weight distributions of F-PETIs were in the range of 1.63–2.37.

Fig. 3 depicts the representative GPC curves of F-PETIs with different Calc'd P_n (1, 2 and 10), in which it can be seen that each imide oligomer was composed of several chemical species with different molecular weights in a broad elution time range. The major molecular weight peaks of F-PETIs were increased with increasing of the Calc'd M_n values. For instance, O10-1 (Calc'd $M_n = 5376$) showed a major elution time peak at 15.1 min, compared with 16.8 min for O2-1 (Calc'd $M_n = 1712$) and 18.2 min for O1-1 (Calc'd $M_n = 1254$), respectively. Moreover, the relative peak intensities in GPC curves were also obviously changed with Calc'd M_n . The higher the Calc'd M_n , the more intensified the peak intensity. For instance, O10-1 showed an intense and broad peak located at 18.8–11.6 min along with several trace peaks, while O1-1

and O2-1 had the major peaks in the relative sharp ranges, implying that O10-1 was mainly consisted of the high-molecular-weight resin species. In quantities, O10-1 has four peaks with different relative intensities: i.e. 34% at 13.1 min, 100% at 15.1 min, 17.5% at 17.5 min, and 10% at 18.3 min respectively, compared with O2-1, which also has four peaks in the elution time range of 12.7–19.1 min: 12% at 13.5 min. 99% at 16.8 min. 100% at 17.5 min and 37% at 18.3 min respectively. Obviously, the major peak intensity was intensified in the higher-molecular weight oligomer. For the oligomers with higher Calc'd M_n (O10-1), the major peak at 15.1 min (100%) was new resin species which was not detected in the lower Calc'd M_n oligomers (O1-1 and O2-1), implying that this new species was coupled by the different lower-molecular molecular resin species. It is obviously that, the molecular weights and molecular weight distributions of F-PETIs were closely related to their designed molecular weights.

Fig. 4 shows the MALDI-TOF mass spectra of the representative imide oligomers with different Calc'd P_n (O1-1, O2-1 and O10-1) and Table 3 summarizes the molecular structures of the resin species detected. The imide oligomers are resin mixtures with different molecular weights. O1-1 and O2-1 showed the same chemical species with identical P_n (0–5) and molecular weights (m/z of 796.7–3087.7), but different 100% peak intensities (O1-1: $P_n = 1$, O2-1: $P_n = 2$). For instance, O1-1, which has the lowest Calc'd P_n (=1), contains 6 resin species with molecular weights ($M_n = 796.7$ to 3087.7) and P_n (0–5): 796.7 ($P_n = 0$, m/z: 819.7–23.0 = 796.7, 1.5%), $1254.4 (P_n = 1, m/z; 1277.4 - 23.0 = 1254.4, 100\%), 1712.4 (P_n = 2, m/z;$ 1735.4-23.0 = 1712.4, 84.7%), 2170.4 ($P_n = 3, m/z$: 2193.4-23.0 = 2170.4, 62.2%), 2628.5($P_n = 4, m/z$: 2651.5-23.0 = 2628.5, 25.5%) and 3087.7 ($P_n = 5$, m/z: 3110.7–23.0 = 3087.7, 6.1%), respectively, in which the species with $P_n = 1$ showed the 100% peak intensity. In comparison, O10-1, which has the highest Calc'd P_n (=10), was composed with as many as 16 chemical species with molecular weights of 965.5-4924.2, in which the 100% peak intensity was detected in the species with $P_n = 3$ (m/z = 2194.4).

Apparently, the major chemical species were polycondensed by the aromatic dianhydride and aromatic diamine along with the endcapping agents. It was also found that double-endcapped chemical species were primarily produced for the lower Calc'd M_n oligomers such as O1-1 and O2-1, and double- and mono-endcapped species were simultaneously formed in the case of the higher Calc'd M_n oligomer (O10-1). In comparing of the effect of Calc'd P_n on the measured molecular weights, it can be concluded that the higher-molecular-weight chemical species were produced with increasing of Calc'd P_n .

3.4. Thermal curing of F-PETIs

Fig. 5 compares the DSC curves of F-PETIs with different Calc'd M_n (O1-1, O2-1 and O10-1) and Table 4 summarizes the DSC data of

Complex melt viscosity of F-PETIs and the unfluorinated derivatives.

Sample	Complex m	Complex melt viscosity (Pa s) at different temperature (°C)				Minimum melt	Melt viscosity	Melt viscosity
	250 °C	280 °C	310 °C	340 °C	370 °C	viscosity (Pa s/°C)	variation at 280 °C for 2 h	variation at 310 °C for 2 h
01-1	15.2	0.4	0.2	0.1	0.2	0.1 at 341 °C	0.46-0.51	0.29-85.7
01-2	83.2	0.9	0.5	0.4	0.7	0.4 at 338 °C	0.65-0.93	0.50-9.75
01–comp	1.9	0.9	0.8	0.8	10.7	0.8 at 320 °C	1.27-2.73	0.88-452
02-1	40.5	4.5	1.6	0.8	3.6	0.8 at 347 °C	3.47-7.25	1.71-134.1
02-2	25.8	4.8	2.4	2.2	31.9	2.3 at 342 °C	4.95-6.44	1.51-87.14
O2–comp	52.1	6.2	3.0	3.1	32.3	2.9 at 324 °C	6.19-7.37	2.93-176.5
010-1	6952	1438	368.7	120.2	65.2	64.8 at 369 °C	-	-
010-2	5498	1213	254.6	55.94	21.6	22.9 at 367 °C	-	-
O10–comp	6803	4684	1204	75.6	83.8	41.7 at 355 °C	-	-

the imide oligomers. The $T_{\rm g}$ s of the imide oligomers determined by DSC were in the range of 136 °C–229 °C. The higher Calc'd $M_{\rm n}$ oligomers showed higher $T_{\rm g}$ values. The strong curing exothermal peaks were observed for the lower Calc'd $M_{\rm n}$ oligomers (O1-1 and O2-1), in which the curing onset temperatures ($T_{\rm onset}$) were measured at 312–323 °C, and the exothermic peaks ($T_{\rm exo}$) at 406–413 °C, respectively. The normalized heat enthalpy (ΔH) was calculated at 139.1–192.6 J/g. However, the higher Calc'd $P_{\rm n}$ oligomer (O10-1) did not show apparently thermal curing exothermal peak, probably due to the low endcapping group density in the long imide chains.

The exothermic peaks of the thermal curing reactions for F-PETIs appeared at 406–441 °C, approximately 10–23 °C higher than the corresponding unfluorinated ones (392–422 °C). This was well accordance with the model compounds, implying that the bulky –CF₃ substituent leaded to steric barrier and resulted in the phenylethynyl group being much difficulty in thermal curing. In addition, the exothermic enthalpy (ΔH) decreased with increasing of the Calc'd P_n . For instance, O10-1 has ΔH of 7.81 J/g, only 5.6% of O2-1 (139.1 J/g) and 4.1% of O1-1 (192.6), respectively. This could be interpreted by the contribution of the low endcapping group density in the higher-molecular weight oligomers.

3.5. Melt processability of F-PETIs

The melt processability of F-PETIs was investigated by the dynamic rheological method. Fig. 6 depicts the typical melt viscosity–temperature curves of the imide oligomers, in which it can be seen that the melt viscosities were decreased gradually with increasing of the scanned temperatures started at 200 °C, then down to a valley stage where the melt viscosity reached the minimum point, and then went up with further increasing of the temperature due to the thermal curing of the fluorinated phenyl-ethynyl groups. Compared with the higher Calc'd M_n oligomers (O2-1 and O10-1), O1-1 showed much broad low viscosity range started from 260 °C to 370 °C, indicating that this oligomer has the widest melt processing window.

The complex melt viscosities at different scanned temperatures and the minimum melt viscosities were summarized in Table 5. Obviously, minimum melt viscosity temperatures were increased with increasing of the molecular weights. For instance, the minimum melt viscosity temperatures were increased from 341 °C (0.1 Pa s) for O1-1–347 °C (0.8 Pa s) for O2-1 and 369 °C (64.8 Pa s) for O10-1. The minimum melt viscosities were also increased gradually with increasing of the molecular weights. Hence, reducing the resin molecular weights could result in sharp decrease in the minimum melt viscosity and widen the processing temperature window. In comparison, O2-1 (Calc'd $P_n = 2$) has the melt viscosity of 0.8 Pa s at 340 °C, the same with O1-*comp* (Calc'd $P_n = 1$), indicating that the higher-molecular-weight F-PETI could give the same low melt viscosity as the low-molecular-weight unfluorinated derivative.

Figs. 7 and 8 show the melt viscosity stabilities of the imide oligomers against the isothermal standing time at 280 °C and 310 °C, respectively. The melt viscosity variations were depended on the resin molecular weights as well as their chemical structures. O1-1 showed the lowest melt viscosity variation of 0.46-0.51 Pa s after isothermal standing at 280 °C for 2 h (Fig. 7), compared with O1-2 (0.65-0.93 Pa s) and O1-*comp* (1.27-2.73 Pa s), implying that the melt stability of the imide oligomers were closely related to their molecular weights as well as the chemical structures derived from the different endcapping agents. At higher isothermal standing temperature (310 °C), the bitrifluoromethyl phenyl-ethynyl-endcapped oligomer (O1-2) showed the best melt viscosity stability than the monotrifluoromethyl phenylethynyl-endcapped



Fig. 7. Isothermal melt viscosity at 280 $^\circ\text{C}$ of the representative F-PETIs and the unfluorinated derivative.

one (O1-1) as well as the unfluorinated phenylethynyl-endcapped one (O1-*comp*). The isothermal standing time (Fig. 8) at which the oligomer melt viscosity abruptly increased was 116 min for O1-2, compared to 89 min for O1-1 and 70 min for O1-*comp*, indicating that the fluorinated phenylethynyl groups showed obvious stabilizing impacts on the oligomer melt viscosity, which is good beneficial to the oligomer melt processability. Overall, the fluorinated phenylethynyl groups would not only contribute to reduce the imide oligomer melt viscosity, but also be beneficial in improving the stability of melt viscosity. These are due to the introduction of the bulky trifluoromethyl in phenylethynyl endcapping groups reduce the interchain interaction and the stiffness of polymer backbone.

3.6. Thermal properties of the thermal-cured polyimides

F-PETIs could be thermally cured at 370 °C for 1 h into the thermoset polyimides. Table 6 summarizes the thermal properties of all cured polyimides determined by DSC and TGA. The T_{gs} of the thermal-cured polyimides are closely related to the oligomer molecular weights. The lower the un-cured oligomer molecular weights, the higher the T_{gs} of the thermal-cured polyimides. For instance, O1-1, with the lowest molecular weight, has the highest T_{gs}



Fig. 8. Isothermal melt viscosity at 310 $^\circ\text{C}$ of the representative F-PETIs and the unfluorinated derivative.

Table 6Thermal properties of the thermal-cured polyimides cured at 370 °C for 1 h

Sample	$T_{g}(^{\circ}C)$	T_{onset} (°C)	T_5 (°C)	$T_{10} (^{\circ}C)$
01-1	332	580	559	598
01-2	321	583	559	598
O1-comp	329	546	555	578
02-1	306	583	561	603
02-2	300	570	546	590
O2-comp	301	552	560	581
010-1	269	578	573	601
010-2	261	577	572	598
O10-comp	263	550	560	575

of 332 °C, 26 °C higher than O2-1 (306 °C), and 63 °C higher than O10-1 (269 °C). Additionally, the monotrifluoromethylphenylethynylendcapped oligomers (O1-1, O2-1 and O10-1) showed a little higher $T_{\rm g}$ s than the bitrifluoromethylphenyl-ethynylendcapped ones (O1-2, O2-2 and O10-2). For instance, the thermal-cured O2-1 has Tg of 306 °C, 6 °C higher than the thermalcured O2-2 (300 °C).

The thermal-cured polyimides provided with the onset decomposition temperatures (T_{onset}) in the range of 570–583 °C, 5% loss temperatures (T_5) of 546–573 °C and 10% loss temperatures (T_{10}) of 578–603 °C (Table 6). No obvious difference in thermal stability in nitrogen was observed for the thermal-cured polyimides. In addition, the thermal-cured fluorinated polyimides exhibited little better thermal stability than the unfluorinated ones. For instance, the thermal-cured O1-1 resin has T_{onset} of 580 °C (34 °C higher than O1-*comp* (546 °C)), and T_{10} of 598 °C (20 °C higher than O1-*comp* (578 °C).

The thermal curing kinetic analysis of the imide oligomers (O1-1, O1-2 and O1-*comp*) were performed using DSC by monitoring of the changes in T_g values as a function of the thermal curing temperatures (360 °C/1 h, 370 °C/1 h, 380 °C/1 h and 390 °C/1 h, respectively). The curing degree (*x*) was calculated by DiBenedetto equation modified for highly crosslinked networks according to the literatures [36,40–43,49]. Applying for the first-order data analysis $(-\ln(1 - x) = K_t)$, the rate constant (*K*) at certain temperature was obtained from the very good line fit. As shown in Fig. 9 in Arrhenius relationship $K = Ae^{-Ea/RT}$ between rate constant and temperature, an activation energy (E_a) of 160.0 kJ/mol for O1-1 and 210.8 kJ/mol for O1-2 were obtained, compared to 141.5 kJ/mol for O1-*comp*. Due to the higher activation energy, O1-2 would have the higher rate



Fig. 9. Arrhenius plots of the thermal curing kinetics of the representative F-PETIs and the unfluorinated derivative.

T	al	ole	7	

Mechanical properties	of the thermal-cured	polyimides at 370	°C/1 h.
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Sample	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
01-1	41.7	1.2	6.2
01-2	39.0	1.4	5.8
O1–comp	47.5	1.3	6.0
010-1	112.2	1.1	18.6
010-2	101.8	1.2	21.2
O10–comp	121.5	1.3	23.5

acceleration trend in the thermal curing reaction than O1-1. And the monotrifluoromethyl phenylethynyl-endcapped oligomer (O1-1) expressed similar thermal curing behavior with the unfluorinated derivative (O1-*comp*).

3.7. Mechanical properties of the thermal-cured polyimides

Table 7 summarizes the mechanical properties of the thermalcured polyimides. After thermally cured at 370 °C for 1 h, the resulted thermoset polyimides with Calc'd $P_n = 1$ (O1-1 and O1-2) exhibited good combined mechanical properties, including tensile strength of 39.0-41.7 MPa, tensile modulus of 1.2-1.4 GPa, elongation at breakage of 5.8–6.2%. The tensile strength and elongation at breakage of the thermal-cured polyimides were greatly improved when the oligomer molecular weights were increased. For instance, the thermal-cured polyimides with Calc'd $P_n = 10$ (010-1, 010-2) showed tensile strength of 101.8-112.2 MPa and elongation at breakage of 18-21%, much better than O1-1 and O1-2. In addition, F-PETIs could produce the thermal-cured polyimides with mechanical properties comparable to the unfluorinated derivatives, revealing that no obvious negative impacts on mechanical properties of the thermal-cured polyimides were observed due to the fluorination of the phenyethynyl groups.

4. Conclusion

Novel fluorinated phenylethynyl-contained endcapping agents, 4-(3-trifluoromethyl-1-phenylethynyl)phthalic anhydride (3F-PEPA) and 4-(3,5-bistrifluoromethyl-1-phenylethynyl)phthalic anhydride (6F-PEPA) have been synthesized, which were employed to synthesize a series of F-PETIs. The experiments on the model compounds indicated that the fluorinated model compounds exhibited 22-35 °C higher in thermal cure temperatures and 42–52% lower in exotherms than the unfluorinated derivative. F-PETIs also holded the thermal curing temperatures of 20-30 °C higher than the corresponding unfluorinated analogues. The melt processability of F-PETIs was apparently improved by the melt viscosities decreased and the melt viscosity stability enhanced due to the -CF₃ groups in the imide oligomers. F-PETIs could be thermally cured at 370 °C to afford the thermal-cured polyimides, which denoted thermal properties with T_g of as high as 332 °C, T_5 of >570 °C, and mechanical properties with tensile strength of as high as 122 MPa, and elongation at breakage of >18%.

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