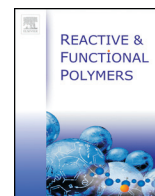




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Synthesis of highly transparent poly(amide–imide)s based on trimellitic acid and dependence of thermal properties on monomer sequence

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ABSTRACT

Transparent, thermally stable, and semiaromatic poly(amide–imide)s were prepared from hydrogenated trimellitic anhydride chloride (h-TAC) with various aromatic diamines. The dependence of thermostability on the monomer sequence and terminal group was investigated. Thermogravimetric/differential thermal analysis (TG/DTA) was performed to evaluate the thermostabilities, which were found to be primarily affected by the monomer sequence in the polymer units. The 5% weight loss temperature (T_{d5}) in N_2 , glass transition temperature (T_g), and cutoff wavelength of the ultraviolet–visible (UV–Vis) spectrum (λ_{cut}) of the semiaromatic poly(amide–imide)s are 422–456 °C, 131–274 °C, and 293–321 nm, respectively, while those of wholly aromatic poly(amide–imide)s are 454–480 °C, 169–287 °C, and 415 nm, respectively.

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1. Introduction

Polyimides (PIs) are a class of polymers that are extensively used in the microelectronics and aerospace industries because of their remarkable properties such as high thermal stability, chemical resistance, good mechanical strength, and excellent insulating ability [1]. However, PIs generally exhibit poor solubility in most organic solvents; thus, the processing must be performed in the soluble poly(amic acid) precursors. Recently, in spite of intractable structures, soluble PIs have been developed by the introduction of bulky substituents [2] or asymmetric kinked structure [3,4]. Two well-known thermoplastic PIs that are used in the mold injection process, poly(amide–imide)s (PAIs) and poly(ether–imide)s (PEIs), were commercialized in 1972 and 1982, respectively. In general, PAI is prepared by the copolycondensation of 4,4'-oxydianiline (ODA), *m*-phenylene diamine (*mpDA*), and trimellitic anhydride chloride (TAC) in an amide solvent. The molded plastic has good thermal properties: glass transition (T_g) of 290 °C and 5% weight loss temperature (T_{d5}) of 470 °C. However, these PEIs still absorb light around 400 nm, making them appear pale yellow, because of the formation of inter- and intramolecular charge transfer complexes; moreover, they have serious processing issues [5–15]. Yang and coworkers studied the preparation of colorless PAIs by decreasing the imide content, changing the monomer sequences, or introducing sulfone group for aromatic amide monomers [16–19]. Recently, semiaromatic or nonaromatic PIs have been developed and used in optoelectronics and as interlayer dielectric materials [20,21] because of their lower coloration,

higher transparency, and lower dielectric constant. Hydrogenated trimellitic anhydride chloride (h-TAC) [22] has been prepared and applied in the synthesis of colorless PEIs with good thermal properties: $T_g = 208$ – 285 °C, $T_{d5}(N_2) = 396$ – 441 °C, ultraviolet–visible (UV–Vis) cutoff wavelength (λ_{cut}) = 292 nm, and 72% transmission at 400 nm [23–25]. Both TAC and h-TAC are asymmetric monomers having highly reactive acid chloride groups and moderately reactive anhydride groups at their terminals. This study describes the synthesis of sequence-controlled PAI by controlling the monomer addition order. The dependence of the thermal and optical properties of PAIs on their microstructure is investigated to develop highly transparent and thermally stable PAIs with or without alicyclic structure.

2. Experimental

2.1. Materials

N,N-dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride. Triethyl amine (TEA) was distilled from potassium hydroxide before use. ODA, *p*-phenylene diamine (*ppDA*), and *mpDA* were purified by sublimation. 4,4'-(9-Fluorenylidene)dianiline (BAFL) and 3,3'-(1,3-phenylenebis(oxy))dianiline (APB) were purified by recrystallization from ethanol. Hydrogenated TAC (mixtures of stereoisomers: *cis/trans* = 6/4) (Mitsubishi Chemical Group Science and Technology Research Center, Inc.) was used as received. 4,4'-Oxydiacetylaniline (ODAA) was prepared according to a previously reported procedure [26]. All other chemicals were used as received.

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2.2. Measurements

Fourier transform infrared (FTIR) spectra were measured on a Jasco FT/IR-4200 spectrometer (Jasco Co. Ltd) by transmittance absorption spectroscopy (KBr tablet method). The number-average molecular weights (M_n), weight-average molecular weights (M_w), and dispersities (M_w/M_n) were determined by a Tosoh HLC-8220 gel permeation chromatograph (GPC), equipped with refractive index and UV detectors, and a consecutive polystyrene gel column (TSK-GEL α -M \times 2), at 40 °C and eluted with *N*-methylpyrrolidone (NMP) at a flow rate of 1.0 mL/min. Nuclear magnetic resonance (NMR) spectroscopy was performed on a Bruker AC-400P spectrometer at 400 MHz for ^1H and 100 MHz for ^{13}C measurements. Deuterated dimethyl sulfoxide (DMSO- d_6) was used as the solvent with tetramethylsilane as the internal reference. Thermal analyses were performed on a HITACHI TG/DTA7220 system at a heating rate of 10 °C/min under air or N_2 . UV-Vis spectra were recorded on a Shimadzu UV spectrophotometer (UV-1800). The films were prepared by casting the solution in DMAc (20 wt%) on a quartz plate, heating at 100 °C on a hot plate, and cooling quickly. Clear transparent films were obtained for the UV-Vis experiment.

2.3. Synthesis of 4-anilinocarbonyl phenyl 1,2-cyclohexane imide

Hydrogenated TAC (2.50 mmol, 0.540 g), aniline (5.00 mmol, 0.465 g), and TEA (2.00 mmol, 0.265 g) were dissolved in DMAc (4 mL) in a two-necked flask under N_2 and the solution was stirred at 30 °C for 2.5 h. Subsequently, pyridine (3.00 mmol, 0.240 g) and acetic anhydride (4.30 mmol, 0.430 g) were added to the reaction solution and the mixture was stirred at 85 °C for 5 h. The reaction solution was then poured into water and the precipitate was filtered and dried under vacuum at 150 °C for 12 h to afford the product as a white powder. Yield: 0.572 g (63%). MP 96.0–97.0 °C. FTIR (KBr, cm^{-1}) 3341 (amide N—H), 3060 (ArC—H), 1779 (imide C=O), 1726 (imide C=O), 1658 (amide C=O), 1597 (ArC=C), 1502 (ArC=C), 1400 (ArC=C), 1380 (imide C—N), 1253 (ether), 1125 (amide C—N). ^1H NMR (400 MHz, DMSO- d_6 , ppm) δ 1.41–1.61 (2H, m, CH_2), 1.70–1.89 (1.5H, m, CH_2), 1.91–1.96 (0.5H, m, CH_2), 2.07–2.25 (2H, m, CH_2), 2.41–2.53 (1H, m, CH), 3.10 (1H, m, CH), 3.28 (0.5H, m, CH), 3.42 (0.5H, m, CH), 7.02 (t, 1H, Ar—H), 7.30 (m, 4H, Ar—H), 7.42 (m, 1H, Ar—H), 7.50 (q, 2H, Ar—H), 7.60 (t, 2H, Ar—H), 9.92 (d, 1H, N—H).

^{13}C NMR (125 MHz, DMSO- d_6 , ppm) δ 20.4, 23.8, 25.0, 28.3, 119.2, 123.1, 127.0, 128.5, 128.9, 132.5, 139.2, 173.2, 178.2, and 178.5.

2.4. Synthesis of PAIs

2.4.1. T–D method

Hydrogenated TAC (2.50 mmol, 0.540 g) was dissolved in DMAc (4 mL) in a two-necked flask under N_2 . The flask was then cooled to -5 °C and ODA (2.50 mmol, 0.500 g) was slowly added. TEA (2.50 mmol, 0.250 g) was then added to the reaction solution and the mixture was stirred for another 0.5 h. The solution temperature was then increased to 30 °C before aniline (2.50 mmol, 0.230 g) was added. The reaction mixture was then stirred at 30 °C for 1 h. Chemical imidization was performed by adding pyridine (3.80 mmol, 0.290 g) and acetic anhydride (7.50 mmol, 0.760 g) to the reaction mixture and holding it at 85 °C for 12 h. The reaction mixture was then poured into methanol and the resulting precipitate was filtered and dried under vacuum at 150 °C for 12 h to afford the target polymer, poly(h-TAC-ODA), as a white powder. Yield: 0.814 g (94%). The other PAI samples were synthesized in a similar manner.

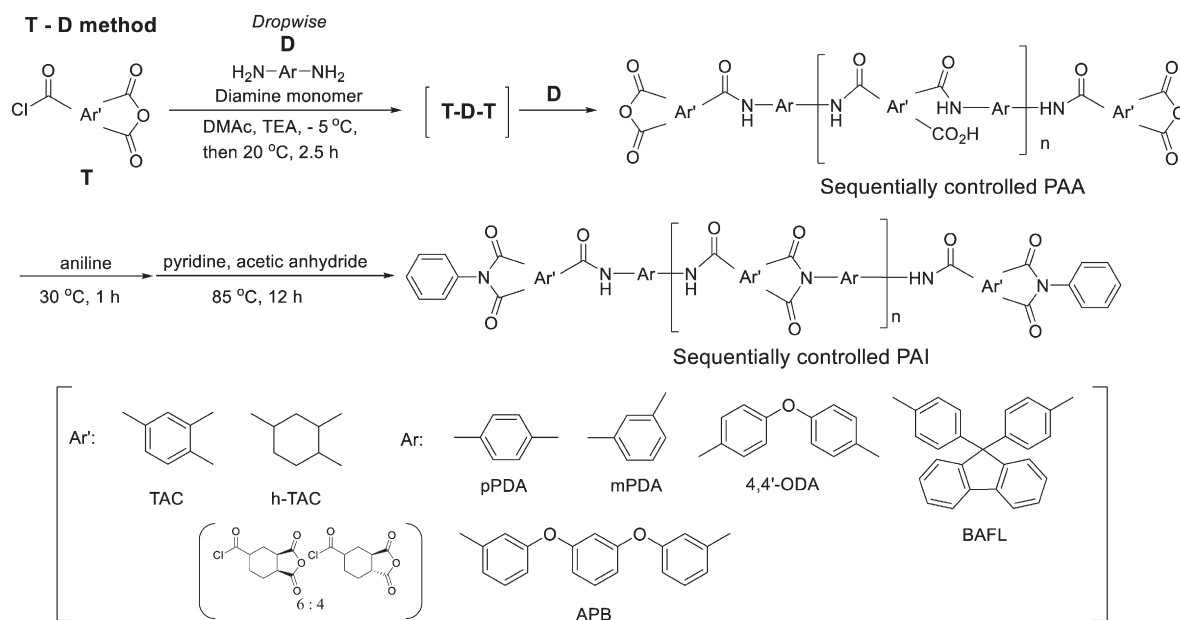
2.4.2. D–T method

ODA (2.50 mmol, 0.500 g) was first dissolved in DMAc (4 mL) in a two-necked flask under N_2 . The flask was cooled to -5 °C, and then h-TAC (2.50 mmol, 0.540 g) was slowly added. The rest of the procedure was exactly the same as in the T–D method described above. Poly(ODA-h-TAC) yield: 0.706 g (78%).

Poly(h-TAC-ODA): FTIR (KBr, cm^{-1}) 3343 (amide N—H), 3061 (ArC—H), 2942 (AlC—H), 1777 (imide C=O), 1708 (imide C=O), 1500 (ArC = C), 1387 (Imide C—N), 1227 (ether), 1169 (amide C—N). ^1H NMR (400 MHz, DMSO- d_6 , ppm): 9.96 (t, 1H, N—H), 7.56 (t, 2H, Ar—H), 7.34 (d, 2H, Ar—H), 7.27 (t, 2H, Ar—H), 7.06 (d, 1H, Ar—H), 6.93 (d, 2H, Ar—H), 3.11 (s, 2H, aliphatic-H), 2.32–1.55 (m, 6H, aliphatic-H).

Poly(h-TAC-pPDA): FTIR (KBr, cm^{-1}) 3343 (N—H), 3061 (ArC—H), 2942 (AlC—H), 1778 (imide C=O), 1708 (imide C=O), 1514 (ArC=C), 1375 (Imide Ph—N), 1177 (amide C—N). ^1H NMR (400 MHz, DMSO- d_6 , ppm): 10.2 (d, 1H, N—H), 7.55 (t, 2H, Ar—H), 2.34–1.55 (m, aliphatic-H).

Poly(h-TAC-mPDA): FTIR (KBr, cm^{-1}) 3345 (N—H), 3061 (ArC—H), 2942 (AlC—H), 1777 (imide C=O), 1709 (imide C=O), 1600 (ArC=C), 1490 (ArC=C), 1375 (Imide Ph—N), 1176 (amide C—N). ^1H NMR (400 MHz, DMSO- d_6 , ppm): 9.97 (t, 1H, N—H), 7.41



Scheme 1. Synthesis of PAI via the T–D method.

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