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Abstract

A series of cardo poly(ether ketone imide)s (PEKI-C) containing large-volume bulky phthalide groups were prepared by aromatic nucleophilic substitution reaction of commercially available phenolphthalein and 4,4’ -bis(4-fluorophthalimido)diphenyl ether/4,4’

Full Text

Synthesis of High-Performance Phenolphthalein-Based Cardo Poly(ether ketone imide)s via Aromatic Nucleophilic Substitution Polymerization

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A series of cardo poly(ether ketone imide)s (PEKI-C) containing large-volume bulky phthalide groups were prepared by aromatic nucleophilic

substitution reaction of commercially available phenolphthalein with 4,4' -bis(4-fluorophthalimido)diphenyl ether and/or 4,4' -difluorobenzophenone. The glass transition temperatures (Tg) increased from 221 to 278 (cid:2)C with increasing content of the 4,4' -bis(4-fluorophthalimido)diphenyl ether moiety in the copolymerization. The 5% weight loss temperatures (T5%) of PEKI-C (a-e) reached up to 472-495 (cid:2)C in nitrogen and 466-481 (cid:2)C in air. Flexible films, which could be easily cast from polymer solutions, exhibited good mechanical properties with tensile strengths of 73-124 MPa, elongations at break of 9.7-12.8%, and tensile moduli of 2.2-2.8 GPa. Their films with cut-off wavelengths from 336 to 368 nm were transparent and essentially colorless. Notably, the Tg, T5%, tensile strengths, elongations at break, and tensile moduli of PEKI-C (a-e) all increased with increasing content of 4,4' -bis(4-fluorophthalimido)diphenyl ether in the copolymerization.

Introduction

Polymers containing cyclic side groups in the backbone of macromolecule repeating units are defined as "cardo polymers," which means "loop" in Latin, because the pendant cyclic groups are considered as loops of the polymer main chain. Compared with conventional linear polymers without side groups, cardo polymers possess enhanced solubility in common organic solvents, higher glass transition temperature, higher softening temperature, higher transmittance in the visible region, and excellent mechanical toughness [1,2].

In recent years, phenolphthalein-based cardo polymers have been most widely studied. Phenolphthalein, which is a commercially available industrial product that can be easily synthesized from phenol and phthalic anhydride [3], is a common pharmaceutical raw material and an important acid-base indicator in analytical chemistry. Many high-performance polymers with phenolphthalein-based cardo groups have been synthesized, including poly(arylene ether sulfone)s (PES-C) [4-14], poly(arylene ether ketone)s (PEK-C) [15-21], poly(benzimidazole) [22,23], and polyetheroxadiazoles [24]. Among these high-performance engineering plastics, PES-C and PEK-C, which possess good solubility, high glass transition temperature, light-colored and fairly transparent optical properties, good thermal-oxidative stability, and excellent mechanical toughness, have been industrialized in China and widely used in many applications such as aerospace, microelectronics, national defense, wire enamels, sterilizable medical equipment, and others [13-15]. The good solubility and transparency of PES-C and PEK-C were attributed to the presence of bulky pendent phthalide groups, which inhibited close packing, thereby increasing the free volume among the molecular chains and reducing interchain interactions. The high glass transition temperature was also due to the bulky phthalide groups, which remarkably improved the rotational energy barrier [13].

Polyimides containing phenolphthalein-based cardo groups have also been studied in recent years, particularly by Yang and coworkers who reported a series of studies on poly(ether imide)s with phthalide cardo groups [25-36]. Compared with conventional linear polyimides, cardo polyimides derived from phenolphthalein-based tetracarboxylic dianhydrides or phenolphthalein-based diamines exhibit better solubility, higher glass transition temperature, and higher transmittance in the visible region. Reddy and coworkers synthesized highly soluble and thermally stable polyimides containing phthalide groups from 3,3-bis(4-aminophenyl)-phthalide [37]. Myung also reported a series of polyimides synthesized from phenolphthalein-based diamines derived from the Williamson ether condensation reaction between phenolphthalein and 4-chloronitrobenzene [38]. Moreover, Hamciuc studied the dielectric properties of poly(ether imide)s derived from phenolphthalein-based tetracarboxylic dianhydride, which was prepared via nitro displacement reaction of 4-nitrophthalonitrile with phenolphthalein in the presence of K2CO3 [39]. Recently, Guo investigated the solubility, thermal, mechanical, and optical properties of a polyimide containing phenolphthalein groups synthesized from a novel phenolphthalein-based diamine [40]. In conclusion, the synthetic routes for polyimides with phthalide cardo groups have involved polycondensation of either phenolphthalein-based tetracarboxylic dianhydrides or phenolphthalein-based diamines. As far as we know, it has not been exploited to prepare cardo poly(ether imide)s by direct aromatic nucleophilic substitution reaction of phenolphthalein with bishalophthalimides. Considering that the introduction of phthalide cardo groups will improve solubility, thermal and mechanical properties, as well as optical properties, in this paper we synthesized and characterized a series of poly(ether ketone imide)s with phthalide cardo groups by direct condensation of phenolphthalein with 4,4’ -bis(4-fluorophthalimido)diphenyl ether and 4,4’ -difluorobenzophenone at different molar ratios. The solubility, thermal stability, mechanical properties, rheological properties, and optical properties of PEKI-C (a-e) were investigated in detail.

2.1. Materials

Phenolphthalein (PP) was purchased from Shanghai Chemical Reagent Plant. 4,4’ -Difluorobenzophenone was kindly supplied by Nanjing Weixun Chemical Co. and used as received. Pyromellitic dianhydride (PMDA) was purchased from Aladdin Chemical Reagent Plant and used as received without further purification. 4,4’ -Diaminodiphenyl ether (4,4’ -ODA) was purchased from Shandong Wanda Chemical Company. N-phenyl-4-fluorophthalimide (4-FPI) was synthesized in our laboratory according to the literature [41]. N,N-Dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (NMP), sulfolane, toluene, and xylene were purified by distillation over calcium hydride and stored over 4 Å molecular sieves. All other reagents for the study were commercially obtained and used as received without further purification.

2.2. Measurements

Fourier transform infrared spectra (FT-IR) were obtained using a Thermo Nicolet 6700 FT-IR spectrometer with samples prepared as KBr pellets. The 1H and 13C NMR spectra were measured at 400 MHz on a Bruker 400 AVANCE III spectrometer using CDCl3 or dimethyl sulfoxide-d6 (DMSO-d6) as solvents. Inherent viscosities (inh) were measured with an Ubbelohde viscometer at 30 ± 0.1 (cid:2)C in DMAc at a concentration of 0.5 g/dL.

Thermogravimetric analysis (TGA) was performed on a PerkinElmer Diamond TG/DTA instrument at a heating rate of 10 (cid:2)C/min under nitrogen and air atmosphere (flow rate of 50 mL/min). Differential scanning calorimetry (DSC) was carried out on a Mettler Toledo DSC at a heating rate of 20 (cid:2)C/min under nitrogen atmosphere with 50 mL/min gas flow, and Tg was obtained at the midpoint of the thermal transition from the second heating. Tensile measurements were tested on at least six PI film specimens (50 mm long, 10 mm wide, and about 0.03 mm thick) using an Instron model 5567 at room temperature, and the results were averaged. Dynamic mechanical thermal analysis (DMTA) was performed on PI film samples (20 mm long, 5 mm wide, and about 0.02 mm thick) on a Mettler Toledo DMA at a heating rate of 3 (cid:2)C/min from 30 to 300 (cid:2)C with a load frequency of 1 Hz in air. Wide-angle X-ray diffraction (WAXRD) measurements were conducted on a Bruker D8 Advance with Cu K radiation at a scanning rate of 5 (cid:2)/min (2 = 5-50 (cid:2)), operated at 40 kV and 40 mA. The melt flow property of polyimides was evaluated using an SRZ 400E melt index instrument (Changchun Intelligent Instrument Equipment Co., Ltd). Melt index (MI) was determined by melting a sample and maintaining it at 330 (cid:2)C for 2 min under a load of 12.5 kg. Elemental analyses were carried out on a PerkinElmer model 2400II C, H, N analyzer. The rheological properties of polyimides were measured using a rotational Physica MCR 301 rheometer (Anton Paar, Austria) in oscillation mode with air flow. The number-average molecular weight (Mn), weight-average molecular weight (Mw), and polydispersity (Mw/Mn) were determined by gel permeation chromatography (GPC) (HLC-8320GPC EcoSEC, Tosoh) with polystyrene calibration using CHCl3 as the eluent at a flow rate of 1.0 mL/min.

2.3. Synthesis of Monomer 4,4'-bis(4-fluorophthalimido)diphenyl ether

In a 500 mL round-bottomed flask equipped with a magnetic stirrer and reflux condenser, 4,4' -oxydianiline (ODA) (20.02 g, 0.10 mol) and acetic acid (300 mL) were added. The mixture was heated until ODA was completely dissolved in acetic acid under nitrogen atmosphere. After addition of 4-fluorophthalic anhydride (33.2 g, 0.20 mol), the mixture was refluxed for 12 h, then cooled to room temperature. The light yellow precipitate was collected by filtration, washed with acetic acid, and dried under vacuum at 150 (cid:2)C for 12 h. 4,4' -Bis(4-fluorophthalimido)diphenyl ether was obtained in 89.6% yield (47.43 g) after recrystallization from toluene/DMAc (v/v = 5:1); m.p. 261-262 (cid:2)C. 1H NMR (DMSO-d6, ppm): 8.07-8.03 (2H, q, J = 4.0 Hz), 7.89-7.87 (2H, dd, J1 = 8.0 Hz, J2 = 2.0 Hz), 7.76-7.71 (2H, t, J = 8.0 Hz), 7.51-7.49 (4H, d, J = 8.8 Hz), and 7.25-7.23 ppm (4H, d, J = 8.8 Hz). FT-IR (KBr): = 1770 (asymmetric C=O stretching), 1718 (symmetric C=O stretching), 1385 (C-N stretching), 738 cm ^{1} (C=O bending), and 1251 cm ^{1} (Ar-O-Ar stretching). Elemental analysis for C28H14N2O5F2 (496.42 g/mol): calcd. C, 67.75%; H, 2.84%; N, 5.64%. Found: C, 67.93%; H, 2.72%; N, 5.56%.

2.4. Synthesis of Polymers

The cardo poly(ether ketone imide)s (PEKI-C) were prepared by solution polycondensation in DMAc. A typical procedure for PEKI-C (c) was carried out as follows: to a 50 mL round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet, and reflux condenser, monomers PP (3.02 g, 0.01 mol), anhydrous K2CO3 (1.52 g, 0.011 mol), xylene (20 mL), and freshly distilled DMAc (20 mL) were added, forming a dark purple solution. When the temperature was raised to 150 (cid:2)C, water began to collect in the Dean-Stark trap. After xylene and water were distilled out, 4,4' -difluorobenzophenone (1.09 g, 5.00 mmol) and 4,4' -bis(4-fluorophthalimido)diphenyl ether (2.48 g, 5.00 mmol) were added. The reaction mixture was gradually heated to 160 (cid:2)C and allowed to react at this temperature for 12 h to finally obtain a viscous solution. Subsequently, 4-FPI (5.20 mg, 0.02 mmol) was added and reacted for another 2 h to obtain 4-FPI end-capped PEKI-C. The solution was then cooled to room temperature and carefully poured into 300 mL ethanol with vigorous stirring to yield a silky precipitate. The precipitate was filtered, washed thoroughly with boiling ethanol several times, and dried at 120 (cid:2)C under vacuum for 8 h. The inherent viscosity of PEKI-C (c) in DMAc at a concentration of 0.5 g/dL at 30 (cid:2)C was 0.42 dL/g. FT-IR (KBr, cm ^{1}): = 1775 (asymmetric C=O stretching), 1715 (symmetric C=O stretching), 1652 (Ar-CO-Ar), 1392 (C-N stretching), 732 (C=O imide ring deformation), and 1250 cm ^{1} (Ar-O-Ar stretching).

Other PEKI-C polymers were synthesized following the same typical procedure:

PEKI-C (a): FT-IR (KBr, cm ^{1}): 1772 (lactone carbonyl), 1650 (Ar-CO-Ar), and 1246 cm ^{1} (Ar-O-Ar stretching).

PEKI-C (b): FT-IR (KBr, cm ^{1}): 1777 (asymmetric C=O stretching), 1718 (symmetric C=O stretching), 1651 (Ar-CO-Ar), 1380 (C-N stretching), and 1248 cm ^{1} (Ar-O-Ar stretching).

PEKI-C (d): FT-IR (KBr, cm ^{1}): 1775 (asymmetric C=O stretching), 1716 (symmetric C=O stretching), 1650 (Ar-CO-Ar), 1386 (C-N stretching), and 1243 cm ^{1} (Ar-O-Ar stretching).

PEKI-C (e): FT-IR (KBr, cm ^{1}): 1779 (asymmetric C=O stretching), 1722 (symmetric C=O stretching), 1385 (C-N stretching), and 1250 cm ^{1} (Ar-O-Ar stretching).

2.5. Polymer Film Preparation

The PEKI-C (a-e) powders were dissolved in DMAc to prepare polymer solutions with a solid content of 10%. These solutions were cast onto clean glass plates, which were placed in an 80 (cid:2)C oven for 8 h to evaporate most of the solvent. The semi-dried PI films were further dried by programmed heating at 100 (cid:2)C for 30 min, 150 (cid:2)C for 30 min, 200 (cid:2)C for 30 min, 250 (cid:2)C for 30 min, and 280 (cid:2)C for 30 min. After cooling naturally to room temperature, the films were stripped from the glass plates by immersion in water. The obtained thin films were about 20-30 m thick and were used for DMTA and tensile measurements.

3.1. Monomer Synthesis

The 4,4' -bis(4-fluorophthalimido)diphenyl ether was prepared in our laboratory by directly reacting ODA with 4-fluorophthalic anhydride, as shown in Scheme 1. A yellow needle-like crystalline monomer was obtained after recrystallization from acetic acid/toluene. The 1H NMR signals corresponding to the central phenyl groups and the 4-fluorophthalimido groups are given in Fig. 1 [Figure 1: see original paper]. Furthermore, the molecular structure of the monomer was confirmed by IR spectroscopy. Characteristic absorption bands were observed at about 1776 (C=O asymmetric stretching), 1721 (C=O symmetric stretching), 1382 (C-N stretching), and 735 cm ^{1} (C=O imide ring deformation). All these data confirmed that the monomer was successfully prepared.

3.2. Polymer Synthesis

As presented in Scheme 2, a series of PEKI-C (a-e) were synthesized via aromatic nucleophilic substitution polymerization. The reaction was conducted in the polar aprotic solvent DMAc using K2CO3 as the catalyst. As shown in Table 1 , the ratio of 4,4' -difluorobenzophenone to 4,4' -bis(4-fluorophthalimido)diphenyl ether was 1:0, 3:1, 1:1, 1:3, and 0:1, and the polymers were coded as a, b, c, d, and e, respectively. The structures of PEKI-C (a-e) were confirmed by IR spectroscopy, with characteristic absorption bands around 1775 (asymmetric C=O stretching), 1714 (symmetric C=O stretching), 1392 (C-N stretching), and 735 cm ^{1} (C=O imide ring deformation) assigned to the imide ring. The absorption band near 1240 cm ^{1} can be assigned to Ar-O-Ar stretching, which derived from the aromatic nucleophilic substitution polymerization of phenolphthalein with 4,4' -bis(4-fluorophthalimido)diphenyl ether and/or 4,4' -difluorobenzophenone.

As shown in Table 1, three possible linkage units (IPI, KPI, KPK) could exist in the polymer chain. As presented in Fig. 2 [Figure 2: see original paper], structural features of PEKI-C (a-e) were confirmed by 13C NMR spectra. Notably, the signal intensity of carbon atoms (C1, C10) in the ketone moiety decreased from polymer a to d, while the signal intensity of carbon atoms (C2, C3, C20, C30) in the imide moiety increased from polymer b to e. This was consistent with the changing ratio of 4,4' -difluorobenzophenone to 4,4' -

bis(4-fluorophthalimido)diphenyl ether in the polymerization. The signal of the aliphatic quaternary carbon in phenolphthalein at about 90.73 ppm was present in all polymers.

3.3. Properties of the PEKI-C (a-e)

3.3.1. Solubility

The qualitative solubility of these polymers was investigated in common organic solvents, and the results are summarized in Table 2 . The PEKI-C polymers exhibit excellent solubility in ordinary organic solvents such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), and m-cresol. The good solubility of these cardo polymers can be explained by the presence of bulky cardo phthalide groups, which create distance between macromolecular chains. The disrupted packing of macromolecular chains facilitates diffusion of small solvent molecules into the polymer matrix, leading to good solubility. The excellent solubility can also be attributed to aromatic ether linkages that increase the flexibility of the polymer backbone [24-35]. Meanwhile, copolymerization is a common but effective method to enhance solubility, as the addition of a second component generally disrupts the regularity of the polymer chain and consequently weakens interchain interactions [41].

3.3.2. Thermal Properties

The thermal decomposition and stability of PEKI-C were evaluated by TGA and DSC, with results shown in Table 3 . All data were obtained from PEKI-C powders. As presented in Fig. 3 [Figure 3: see original paper], the Tg values ranged from 221 to 278 (cid:2)C and increased in the order $a < b < c < d < e$, demonstrating a general trend that Tg values increased with increasing phthalimide unit content in the polymer backbone. This phenomenon occurred because the five-membered heterocyclic phthalimide unit is much more rigid and has stronger interchain interactions than the benzophenone unit.

As shown in Table 3, the T5% values of PEKI-C (a-e) in nitrogen remained in the range of 472-495 (cid:2)C, while the T5% values in air were in the range of 466-481 (cid:2)C.

3.3.3. Mechanical Properties

The mechanical properties of PEKI-C (a-e) films are listed in Table 3. The PEKI-C films, approximately 20 m thick, exhibited good mechanical properties with tensile strengths of about 100 MPa, elongations at break exceeding 9.7%, and tensile moduli exceeding 2.2 GPa. Notably, the tensile strengths, elongations at break, and tensile moduli increased with increasing phthalimide unit content, which effectively contributed to enhanced interchain interactions [27,28].

3.3.4. Dynamic Mechanical Properties

The dynamic mechanical analysis spectra of PEKI-C (a-e) are presented in Fig. 4 [Figure 4: see original paper]. The excellent storage moduli (E') were maintained at about 2.3 GPa almost completely before reaching the corresponding Tg values. The peak temperature in the tan curves was regarded as the glass transition temperature, with Tg values for these PEKI-C polymers increasing in the order: a (218 (cid:2)C) < b (243 (cid:2)C) < c (257 (cid:2)C) < d (269 (cid:2)C) < e (275 (cid:2)C), which were slightly lower than those measured by DSC.

3.3.5. Optical Properties

The optical transparency of PEKI-C (a-e) films was evaluated by visual inspection and UV-vis spectroscopy. Fig. 5 [Figure 5: see original paper] shows photographs of these films. Notably, the films were transparent and essentially colorless, which is significantly different from the deep yellow or brown color of traditional aromatic polyimide films derived from pyromellitic dianhydride (PMDA) and 4,4' -oxydianiline (ODA).

Typical UV-visible spectra of these films are illustrated in Fig. 6 [Figure 6: see original paper], and the cut-off wavelengths (absorption edge) and transmittance at 400, 450, and 500 nm from the UV-visible spectra are summarized in Table 4 . As expected from the nature of the bulky cardo phthalide groups, all films exhibited excellent optical transparency, with UV cut-off wavelengths shorter than 368 nm and transmittance at 450 nm higher than 81%. This contrasts sharply with typical aromatic polyimide film derived from PMDA and ODA, which showed a deep yellow color with 0 of 445 nm and transmittance at 450 nm of only 2%. The excellent optical transparency of these films was attributed to incorporation of bulky cardo phthalide groups in the polymer structure, which inhibited close packing, thereby increasing free volume among molecular chains and effectively suppressing inter- and intramolecular charge transfer interactions [27,28]. When comparing the coloration of these films, it was interestingly observed that optical transparency increased slightly with decreasing phthalimide unit content in the polymer backbone. Specifically, 0 decreased in the order e > d > c > b > a, while transmittance at 400 nm (from 44% to 82%) and at 450 nm (from 81% to 86%) increased in the order e < d < c < b < a. This phenomenon was likely attributed to the decreasing content of the five-membered heterocyclic phthalimide unit, which effectively contributed to inter- and intramolecular charge transfer interactions [27,28].

3.3.6. XRD

As shown in Fig. 7 [Figure 7: see original paper], the morphological structures of PEKI-C (a-e) were evaluated by wide-angle X-ray diffraction measurements. The XRD spectrum of Kapton polyimide shows three peaks at 15.10°, 22.44°, and 26.12° with the most intense peak appearing at 15.10°. In contrast, most

PEKI-C films exhibited typical Gaussian distribution curves that were broad and amorphous, suggesting that all PEKI-C (a-e) polymers were amorphous. The amorphous nature of these cardo polyimides could be attributed to the introduction of large-volume phthalide groups, which resulted in loose chain packing and aggregation. Meanwhile, copolymerization effectively disrupted the regularity of the polymer main chain.

3.3.7. Rheological Behavior

The melt index and rheological properties of PEKI-C (a-e) were studied in detail. All PEKI-C (a-e) samples were obtained as PI powders, and their inherent viscosities were controlled to similar molecular weights (about 0.40 dL/g) using the end-capping agent N-phenyl-4-fluorophthalimide. As presented in Table 5 , the Mn of this series of PEKI-C (a-e) was about 10,000 g/mol, while Mw was approximately 20,000 g/mol. The complex viscosity was measured using a rotational rheometer over the temperature range of 300-400 (cid:2)C. Data were collected at a frequency of 1 Hz, a strain of 3%, and a heating rate of 3 (cid:2)C/min. Complex viscosity represents the viscosity of melted polymers and is related to melt processability. Fig. 8 [Figure 8: see original paper] displays the rheological behavior of PEKI-C (a-e). The complex viscosities decreased dramatically above Tg for all polymers, consistent with the rapid softening of their films observed in DMTA tests. The complex viscosity of PEKI-C (a) was the lowest among these polymers over a wide temperature range, with a minimum complex viscosity of about 4403 Pa · s at 342 (cid:2)C. Furthermore, as summarized in Table 5, the minimum complex viscosity of PEKI-C (a-e) decreased with decreasing phthalimide unit content, following the order: e > d > c > b > a, which was consistent with the MI trend measured by the SRZ 400E melt index instrument. This rheological behavior occurred because the five-membered heterocyclic phthalimide unit is much more rigid and has stronger interchain interactions than the benzophenone unit.

4. Conclusion

A series of cardo poly(ether ketone imide)s (PEKI-C) (a-e) containing large-volume phthalide groups were synthesized and characterized. All cardo polymers exhibited excellent solubility in ordinary organic solvents, which can be explained by the presence of large-volume cardo phthalide groups. The Tg values increased from 221 to 278 (cid:2)C with increasing phthalimide unit content in the polymer backbone. Dynamic mechanical analysis demonstrated that excellent storage moduli were maintained almost completely before reaching the corresponding Tg values. The minimum complex viscosity decreased with decreasing phthalimide unit content, following the order: e > d > c > b > a. The good optical transparency of these PEKI-C (a-e) films was associated with incorporation of large-volume cardo phthalide groups into the polymer backbone, which inhibited close packing, thereby increasing free volume among molecular chains and reducing interchain interactions. These data demonstrate that this novel class of cardo poly(ether ketone imide)s, endowed with good solubility, high thermal stability, and good optical transparency, can serve as high-performance optical materials, where properties can be tuned by controlling the ratio of 4,4' -bis(4-fluorophthalimido)diphenyl ether to 4,4' -difluorobenzophenone.

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