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Flexible, low-colored and transparent thin films prepared from new thermo-stable and organo-soluble poly(amide-imide)s

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ABSTRACT

An imide ring-containing diacid, 2,2′-diphenyl-4,4′-bis(N-trimellitoyl)diphenyl ether (PTPE) was synthesized through a three-step pathway starting from 2,2′-diiodo-4,4′-dinitrodiphenyl ether. A series of novel aromatic poly(amide-imide)s having bulky phenyl pendant groups at 2,2′-disubstituted positions were then prepared via a direct phosphorylation polycondensation between PTPE and various aromatic diamines. Chemical structure of the new monomer as well as the resulted polymers was thoroughly confirmed by IR and NMR spectroscopic methods. Intrinsic viscosities [η] of the polymer solutions at 25 °C were measured by the extrapolation of their viscosity numbers till zero concentration. $\overline{M_w}$ and $\overline{M_n}$ values of the resulting polymers were determined using gel-permeation chromatography (GPC). The polymers showed a good film-forming ability, and some characteristics of their thin films including color and flexibility were investigated qualitatively. In addition, the absorption edge values (λ_0) obtained from their UV curves were determined, and all the resulting poly(amide-imide)s films exhibited high optical transparency. Thermal stability of the polymers using their TGA thermograms was investigated. The T_g values of the poly(amide-imide)s obtained from their DSC plots were also quantified. Crystallinity amount of the prepared macromolecules was evaluated using wide-angle X-ray diffraction (XRD). Furthermore, solubility of the samples in a variety of organic solvents including dimethyl sulfoxide (DMSO), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), pyridine, tetrahydrofuran (THF), and toluene was tested.

1. Introduction

Aromatic polyamides, polyimides, and poly(amide-imide)s are well known as high performance polymers, which possess excellent thermal stability, chemical resistance, and mechanical strength [1–5]. However, in addition to these useful properties, for many applications polymers need to have good film-forming ability and adequate organo-solubility [6–8]. In order to answer these requirements, structural modifications of polymers often become essential. It has been observed that introduction of bulky aromatic substituents such as phenyl [9–11], naphthyl [12], biphenyl [13], phenoxy [14], anthracene [15], and pyrene [16] can impart many of these desirable properties to the polymers, making them suitable for a much wider range of applications. In 2005, Morikawa et al. reported the synthesis of a series of polyimides obtained from 2,2′-diphenyl-4,4′-diaminodiphenyl ether (PAPE) and various kinds of dianhydrides [17]. The used complicated five-step pathway to synthesize PAPE has been recently modified in our research laboratory by a simple three-step method [18]. In this modified manner, the mentioned diamine has been synthesized starting from 4,4′-dinitrodiphenyl ether and iodine to yield 2,2′-diiodo-4,4′-dinitrodiphenyl ether (INPE) via an electrophilic aromatic substitution reaction, followed by the Suzuki coupling reaction of INPE with phenylboronic acid to give 2,2′-diphenyl-4,4′-dinitrodiphenyl ether (PNPE), and finally by a catalytic reduction of PNPE using hydrazine monohydrate and Pd/C in ethanol. In fact, an analog of the above three-step pathway has been previously carried out for the synthesis of a diamine containing phenoxyphenyl arms namely 2,2′-bis[(*p*-phenoxyphenyl)]-4,4′-diaminodiphenyl ether (PPAPE) [19,20]. If we give attention to the synthesis routes of PAPE and PPAPE we can conclude an economical preference for the synthesis of PAPE relative to PPAPE. Phenylboronic acid as an initial substance of PAPE is more available and cheaper than the starting material of PPAPE namely 4-phenoxyphenylboronic acid. Consequently, although PAPE has two smaller laterally-attached groups (phenyl in comparison with *p*-phenoxy phenyl in PPAPE), a relatively convenient method can be utilized for its preparation. Thereby, the aromatic polymers obtained from diamine PAPE instead of PPAPE

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are certainly more desirable because of their facile preparation. On the other hand, replacement of polyimides by copolyimides such as poly(amide-imide)s may be useful in modifying the intractable nature of polyimides. Poly(amide-imide)s seems to provide a favorable balance between processability and performance [21–26]. The present work deals with the synthesis of an imide ring-containing diacid namely 2,2′-diphenyl-4,4′-bis(N-trimellitoyl)diphenyl ether (PTPE) from diamine PAPE. The poly(amide-imide)s obtained from PTPE were characterized by IR, NMR, intrinsic viscosity, GPC, thin film characteristics, TGA, DSC, and their organo-solubility.

2. Experimental

2.1. Materials

All chemicals were purchased from Merck and Fluka Chemical Co. Trimellitic anhydride (TMA) and triphenyl phosphate (TPP) were used as received. Reagent-grade calcium chloride was dried under vacuum at 180 °C before use. N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves. Benzidine (BEZ) was of high purity when received and was used without any further purification. 4,4′-Oxydianiline (ODA) was purified by recrystallization from ethanol before use. 2,2′-Diphenyl-4,4′-diaminodiphenyl ether (PAPE) was synthesized during the synthesis of the diacid monomer PTPE by a procedure reported elsewhere [18]. 1,5-Bis(2-amino-4-trifluoromethylphenoxy)naphthalene (AFPN) was synthesized by the condensation reaction of 1,5-dihydroxynaphthalene with 4-chloro-3-nitrotrifluoromethyl benzene, followed by the reduction of the intermediate dinitro compound. Details of the synthesis of diamine AFPN were similar to that of reported in literature [27].

2.2. Measurements

Intrinsic viscosity data were measured using an Ubbelohde viscometer with polymer solutions in DMAc at 30 °C. Melting points were determined in open capillaries with IA 9200 Series Digital Melting Point apparatus. FT-IR spectra were recorded on a PERKIN ELMER RX I FT-IR spectrometer. The spectra of solids were obtained using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DPX-500 500-MHz spectrometer using dimethyl sulfoxide-d_6 (DMSO-d_6), and tetramethylsilane was used as an internal standard. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a Mettler TA 5000 system (Columbus, OH) under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Weight- and number-average molecular weights of the resulting poly(amide-imide)s were determined by gel-permeation chromatography (GPC). This chromatography was performed on a Waters 150-C instrument using Styragel columns and a differential refractometer detector. The molecular weight calibration was carried out using polystyrene standards. Calibration and measurements were made at a flow rate of 1 mL min^{-1} with tetrahydrofuran (THF) as the eluent. Ultraviolet maximum wavelength (λ_{max}) values were determined with a GBC model 916 ultraviolet–visible (UV–Vis) instrument (GBC Scientific Equipment, Australia) in DMSO at a concentration of 10^{-5} mol L^{-1}. Cut-off wavelength (absorption edge) values (λ_0) of the prepared thin films were determined with a PERKIN ELMER PTP-1 Peltier System Lambda 25 UV/VIS Spectrometer. Wide-angle X-ray diffraction patterns were performed at room temperatures with film specimens on a Bruker Advance D5 X-ray diffractometer with Ni-filtered Cu/Ka radiation (30 kV, 25 mA).

2.3. Synthesis of 2,2′-diphenyl-4,4′-bis(N-trimellitoyl)diphenyl ether (PTPE)

A round-bottomed flask equipped with magnetic stirrer and reflux condenser was charged with diamine PAPE (1.7622 g, 5 mmol), trimellitic anhydride (2.3055 g, 12 mmol), and glacial acetic acid (25 ml). The resulting heterogeneous mixture was then refluxed for 15 h. Next, it was filtered to yield a yellow solid, which was rinsed with ethanol to remove acetic acid. The obtained crude product was recrystallized from DMF/H_2O (1:1), and then dried in vacuum at 100 °C for 24 h to afford 3.0128 g (86%) of monomer PTPE, mp = 306–308 °C.

2.4. Preparation of poly(amide-imide)s

A typical example of the phosphorylation polycondensation reactions is as follows. A mixture of diacid PTPE (1.4013 g, 2 mmol), diamine ODA (0.4005 g, 2 mmol), calcium chloride (0.96 g), pyridine (2.4 ml), triphenyl phosphate (TPP) (1.6 ml), and NMP (10 ml) was heated with stirring at 100 °C for 3 h. The viscosity of the reaction solution increased after 1 h, and an additional NMP (5 ml) was added to the reaction mixture. The viscous polymer solution obtained was trickled on stirred methanol to give rise to a crude precipitate, which was washed thoroughly with methanol and hot water, collected by filtration, and dried in a vacuum at 100 °C for 24 h to afford 1.6778 g (97%) of poly(amide-imide) PTPE/ODA as yellow solid. All other polymers were prepared in a similar manner.

3. Results and discussion

3.1. Synthesis

Scheme 1 shows the synthetic route to diimide-diacid PTPE by the ring-opening addition of diamine PAPE and trimellitic anhydride in refluxing glacial acetic acid to yield the corresponding di(amic-acid) intermediate, followed by the intramolecular cyclodehydration of this intermediate to give rise to the related cyclic imide groups. Fig. 1 (top) displays the FT-IR spectrum of monomer PTPE. This spectrum showed the characteristic absorption bands around 2500–3400 cm^{-1} (–OH, carboxylic acid), 1780 cm^{-1} (imide C═O asymmetrical stretching), and 1725 cm^{-1} (imide C═O symmetrical stretching and acid C═O stretching), confirming the presence of imide ring and carboxylic acid groups in the structure. As shown in Fig. 1 (middle), the ^{1}H NMR spectrum of PTPE presented three proton signals around the downfield regions (8.07–8.42 ppm) due to the trimellitic acid moiety. Like many other cases, here too the protons of the carboxylic acid groups were not detected probably due to their fast exchange with a trace amount of moisture associated with solvent DMSO-d_6 [28]. The ^{13}C NMR spectrum of PTPE exhibited 16 peaks of various absorptions for every aromatic carbon. In this spectrum, carbonyl carbons of carboxylic acid and imide groups were observed at 163.2 and 166.9 ppm, respectively. Fig. 1 (bottom) shows the ^{13}C NMR spectrum of PTPE.

Indeed, the imide ring-containing diacid PTPE has been designed as a potentially suitable monomer for poly(amide-imide)s, capable of imparting good processability and high thermal stability at the same time. According to the phosphorylation technique first described by Yamazaki et al. [29,30], a series of novel poly(amide-imide)s with laterally-attached phenyl groups were synthesized from the diacid PTPE and various diamines as shown in Scheme 2. All the polycondensations were homogeneous throughout the reactions and afforded highly viscous polymer solutions with up to 95% yield. Intrinsic viscosity [η] values of the resulting poly(amide-imide)s in DMAc at 30 °C as well as the results of GPC analyses are tabulated in