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Synthesis and characterization of organo-soluble thioether-bridged polyphenylquinoxalines with ultra-high refractive indices and low birefringences

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ABSTRACT

Two aromatic tetraketones, 4,4′-thiobis[(*p*-phenyleneoxy)benzil] (STK, 1) and 4,4′-thiobis[(*p*-phenylenesulfanyl)benzil] (3STK, 2) were synthesized by the nitro nucleophilic substituent reactions of 4-nitrobenzil and corresponding diol compounds. The two tetraketones were polymerized with three aromatic tetraamines, including 3,3′-diaminobenzidine (a), 3,3′,4,4′-tetraaminodiphenylether (b) and 3,3′,4,4′-tetraaminodiphenylsulfone (c), respectively to afford six thioether-bridged polyphenylquinoxalines (PPQs) – PPQ-1a–1c and PPQ-2a–2c. The obtained PPQs exhibited good solubility not only in conventional *m*-cresol and chloroform, but in the aprotic solvent – *N*-methyl-2-pyrrolidinone (NMP). PPQ-1c and 2c containing sulfone units were even soluble in tetrahydrofuran at room temperature with a solid content of 15 wt%. Flexible and tough PPQ films cast from their NMP solution showed good thermal stabilities, including glass transition temperatures in the range of 215–248 °C and 5% weight loss temperatures exceeding 500 °C in nitrogen. The PPQ films at a thickness of ~10 μm exhibited moderate optical transparency at 450 nm. The best optical transmittance around 80% was achieved by PPQ-1c and 2c containing electron-withdrawing sulfone moieties. The synergic effects of flexible thioether linkages and highly conjugated quinoxaline rings in the present PPQs endowed them with ultra-high refractive indices up to 1.7953 at 632.8 nm and birefringences close to zero.

1. Introduction

High refractive index (high-*n*) polymers have currently attracted much attention in fabricating high performance optoelectronic devices [1,2]. Polymer coatings with refractive index (*n*) higher than 1.70 are promising materials for a wide range of optoelectronic applications due to their great potential in improving the performance of the devices [3–6]. However, the *n* values of conventional polymers are usually lower than 1.70 [7]. Based on Lorentz–Lorenz equation [1], various methodologies have been now established to increase the *n* values of polymers beyond 1.70, including introduction of sulfur elements, halogens except fluorine, phosphorous components, metallic elements as well as other substituents with high molar refractions (R_M) and low molar volumes (V_M). Among the substituents, sulfur-containing groups, such as linear thioether (–S–), cyclic thioether (thiophene, thianthrene or thiadiazole) and sulfone ($-SO_2-$), seem to be the most optimal choices due to their combined advantages to develop high-*n* optical polymers. Thus, various sulfur-containing polymers, including poly(arylene sulfide), poly(ether sulfone), and poly(thioether ketone) [8–10] have been well investigated as high-*n* optical materials. In addition, aromatic, particularly heteroaromatic components are also beneficial to increase the polymers' *n* values. For instance, Ueda lab developed a series of sulfur-containing polyimides possessing *n* values as high as 1.77 at 632.8 nm [11–16].

Polyphenylquinoxaline (PPQ) is an important class of heteroaromatic polymer, first developed by Hergenrother in 1967 [17]. PPQ is characterized by its low moisture absorption, high thermal and hydrolytic stability; thus initially developed to serve as high-temperature repellent adhesives or composites to meet the severe demands of extreme environments [18–20]. Lately, various specific properties of PPQs have been gradually revealed, greatly expanding their applications in high-tech fields. Up to now, PPQs with various structural characteristics and functionalities have been developed. Systemic work includes the low-cost PPQs synthesized from self-polymerizable quinoxaline monomers developed by Harris group [21–25]; sulfonated PPQs for proton exchange membrane fuel cells [26,27]; and nanoporous PPQ foams as potential low-*k* interlayer dielectric materials for integrated circuit [28,29]. Recently, the applications of PPQs in optical fields have been increasingly investigated. Various electron-transporting PPQs [30–32] and nonlinear optical PPQs [33,34] were reported.

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Although PPQs have been widely evaluated as optical materials, to our knowledge, researches concerning refractive indices of the polymers have rarely been addressed until now. Actually, from the viewpoint of structure characteristics, there exists a high content of aromatic components with high molar refractions in PPQs, which might be propitious to increasing their *n* values. This fact attracted us to investigate the structure–refractive index relationships in PPQs. Our preliminary research has confirmed that ether-containing PPQs exhibited intrinsic high refractive indices and low birefringence [35]. Thus, as a part of our continuous endeavor to develop high-*n* polymers, the objective of the present work is to further increase the *n* values of PPQs by introduction of sulfur units. Meanwhile, the optical transparency of the PPQs in ultraviolet–visible light region was also taken into consideration. The synergic effects of thioether and quinoxaline ring on the solubility, thermal stability, especially refractive index and birefringence of the PPQs were investigated in detail.

2. Experimental

2.1. Materials

4-Nitrobenzil was synthesized in our laboratory according to the literature [36]. 4,4′-Thiobisbenzenethiol, 4,4′-thiodiphenol and 3,3′-diaminobenzidine (a) were purchased from Aldrich Chemical Co. and used as received. 3,3′,4,4′- Tetraaminodiphenylether (b) was synthesized according to the reported procedure [37]. 3,3′,4,4′-Tetraaminodiphenylsulfone (c) was kindly supplied by Konishi Chemical Ind. Co., Japan and recrystallized from acetonitrile before use. *N*-methyl-2-pyrrolidinone (NMP), dimethylsulfoxide (DMSO), *m*-cresol, *N*,*N*-dimethylacetamide (DMAc), cyclopentanone (CPA), tetrahydrofuran (THF) and other solvents were purified by distillation prior to use. The other commercially available reagents were used without further purification.

2.2. Measurements

Inherent viscosity was measured using an Ubbelohde viscometer with a 0.5 g/dL NMP solution at 25 °C. Absolute viscosity was measured using a Brookfield DV-II+ Pro viscometer at 25 °C. Gel permeation chromatography (GPC) measurements were performed using a Waters 1515 HPLC pump equipped with a Waters 2414 refractive index detector. Two Waters Styragel columns (HR 5E) kept at 35 °C ± 0.1 °C were used with HPLC grade tetrahydrofuran (THF) as the mobile phase at a flow rate of 1.0 mL/min. Fourier transform infrared (FT IR) spectra were obtained with a Tensor 27 Fourier transform spectrometer. Ultraviolet–visible (UV–vis) spectra were recorded on a Hitachi U-3210 spectrophotometer at room temperature. The cutoff wavelength was defined as the point where the transmittance drops below 1% in the spectrum. Prior to test, PPQ samples were dried at 100 °C for 1 h to remove the absorbed moisture. Nuclear magnetic resonances (^{1}H NMR and ^{13}C NMR) were performed on a AV 400 spectrometer operating at 400 MHz in DMSO-d_6 or $CDCl_3$. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a TA-Q series thermal analysis system at a heating rate of 10 °C/min and 20 °C/min in nitrogen or air, respectively. The tensile properties were performed on an Instron 3365 Tensile Apparatus with 80 × 10 × 0.05 mm^3 specimens in accordance with GB 1447-83 at a drawing rate of 2.0 mm/min. Seven samples of each PPQ film were tested. Dielectric constants (ε) were measured on a QBG-3B high-frequency Q meter in accordance with GB 1409-88 at 1 MHz at room temperature. Samples were dried at 120 °C for 1 h to eliminate absorbed moisture prior to testing.

Solubility was determined as follows: 1.5 g of the PPQ resin was mixed with 8.5 g of the tested solvent at room temperature (15 wt% solid content), which was then mechanically stirred in nitrogen for 24 h. The solubility was determined visually as three grades: completely soluble (++), partially soluble (+), and insoluble (−). The complete solubility is defined as a homogenous and clean solution is obtained, in which no phase separation, precipitation or gel formation is detected.

Refractive index of the PPQ film formed on a 3-inch silicon wafer was measured at room temperature with a prism coupler (Metricon, model PC-2010) equipped with a He–Ne laser light source (wavelength: 632.8 nm). The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive index were determined using linearly polarized laser light parallel (transverse electric, TE) and perpendicular (transverse magnetic, TM) polarizations to the film plane, respectively. In-plane (n_{TE})/out-of-plane (n_{TM}) birefringence (Δn) was calculated as a difference between n_{TE} and n_{TM}. The average refractive index (n_{av}) was calculated according to equation (1):

$$n_{av} = (2n_{TE} + n_{TM})/3 \quad (1)$$

2.3. Monomer synthesis

2.3.1. 4,4′-Thiobis[(p-phenyleneoxy)benzil] (STK, 1)

In a 500-mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and a condenser, a mixture of 4-nitrobenzil (53.60 g, 0.21 mol), 4,4′-thiodiphenol (21.8 g, 0.1 mol), and anhydrous DMSO (240 mL) was heated to 60 °C. Then, anhydrous potassium carbonate (69.11 g, 0.5 mol) was added. The reaction was maintained at 60 °C for 20 h. Upon confirmation of the completion of the reaction by thin-layer chromatography, the solution was cooled to room temperature and then poured into a mixed solvent containing hydrochloric acid (1 mol/L, 2400 mL) and chloroform (600 mL). The organic phase was collected and washed thoroughly with deionized water. Then, the chloroform solution was dried with $MgSO_4$. After distilling off the solvent, a pale-yellow solid was obtained. The crude product was purified by a two-step recrystallizations, first from acetic acid and then from a mixture of benzene–ethanol (4:3, v/v). The purified tetraketone STK was obtained as pale-yellow crystals (39.55 g, yield: 62.3%).

Melting point: 127.5 °C (DSC peak temperature). FT IR (KBr, cm^{-1}): 1672, 1600, 1582, 1483, 1248, 1163 and 881. ^{1}H NMR ($CDCl_3$): 7.04–7.08 (m, 8H), 7.39–7.42 (d, 4H), 7.51–7.55 (t, 4H), 7.66–7.70 (t, 2H), and 7.97–7.99 (m, 8H). ^{13}C NMR ($CDCl_3$): 117.3, 120.6, 127.4, 128.5, 129.4, 131.4, 131.9, 132.5, 132.6, 134.4, 153.9, 162.5, 192.4, and 193.9. Mass [m/e (relative intensity)]: 529 (M^+-105, 100). Elemental analysis: calculated for $C_{40}H_{26}O_6S$: C, 75.70%; H, 4.13%. Found: C, 75.46%; H, 4.09%.

2.3.2. 4,4′-Thiobis[(p-phenylenesulfanyl)benzil] (3STK, 2)

The monomer was similarly synthesized by the procedure as STK except that 4,4′-thiobisbenzenethiol was used instead of 4,4′-thiodiphenol.

Melting point: 158.9 °C (DSC peak temperature). FT IR (KBr, cm^{-1}): 1666, 1585, 1473, 1215, 1176 and 878. ^{1}H NMR (DMSO-d_6): 7.35–7.37 (d, 4H), 7.45–7.47 (d, 4H), 7.55–7.57 (d, 4H), 7.60–7.64 (t, 4H), 7.77–7.81 (t, 2H), 7.84–7.86 (d, 4H), and 7.89–7.91 (d, 4H). ^{13}C NMR ($CDCl_3$): 127.6, 129.0, 129.9, 130.4, 130.7, 132.0, 132.9, 134.7, 134.9, 136.6, 147.1, 193.3, and 194.3. Mass [m/e (relative intensity)]: 561 (M^+105, 100). Elemental analysis: calculated for $C_{40}H_{26}O_4S_3$: C, 72.05%; H, 3.93%. Found: C, 71.76%; H, 3.88%.

2.4. Polymer synthesis and film preparation

Six PPQs, including PPQ-1a–1c based on STK and PPQ-2a–2c based on 3STK were synthesized via a two-step procedure with *m*-cresol as the solvent (Scheme 2). As a typical embodiment,