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Polymer 46 (2005) 5903–5908
polymer
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Synthesis and characterization of polyimides with low dielectric constants from aromatic dianhydrides and aromatic diamine containing phenylene ether unit

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Received 25 March 2005; accepted 6 May 2005
Available online 15 June 2005

Abstract

New aromatic polyimides (PIs) having the lowest dielectric constant in nonfluorinated PIs have been developed from aromatic dianhydrides and an aromatic diamine containing phenylene ether units. The diamine monomer was prepared from 4-bromophenyl ether in five steps. Polycondensations were performed in 1-methyl-2-pyrrolidinone at room temperature for 18 h, giving poly(amic acid)s (PAAs) with inherent viscosities up to 0.53 dl/g. PAAs were converted to corresponding poly(imide)s (PIs) by thermal treatment at 300 °C. New PIs showed good thermal stability (5% weight loss around 450 °C) and the low dielectric constant (2.74).

Keywords: Polyimide; Phenylene ether; Dielectric constant

1. Introduction

Polyimides (PIs) are used as protection and insulation materials in microelectronics, because they possess good thermal and mechanical stability, solution processability, and low dielectric constants (ε) [1]. In microelectronic device circuit, the propagation velocity of the signal is inversely proportional to the square of ε of the propagation medium. Therefore, materials with the low ε are required for faster signal propagation in microelectronic devices without cross-talk in new multilevel high-density and high-speed electronic circuits.

Recently, Goto et al. [2,3] reported low ε and thermally stable PI with fluorene structure, which has the lowest ε in the nonfluorinated PIs. Introducing aromatic bulky fluorene moieties into PI structure is effective to lower the ε with keeping its superior thermal stability due to decreasing both the density of the polymer and the imide group concentration per repeating units [4]. It is of interest to develop another connecting unit between imide groups to produce PIs with low ε.

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE), a typical engineering plastic, is well known as a low ε material ($\varepsilon = 2.5$) [5–7]. PPE is prepared by oxidative coupling polymerization of 2,6-dimethylphenol with a copper-amine catalyst, which is an atom-economical polymerization because the side product is only water. These findings prompted the development of new nonfluorinated PIs with the very low ε by introducing phenylene ether units in the main chains.

This report describes the synthesis and properties of novel nonfluorinated PIs with the very low ε from aromatic dianhydrides and an aromatic diamine containing phenylene ether units.

2. Experimental section

2.1. Materials

1-methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylformamide (DMF) were purified by the usual manner, and stored under an atmosphere of N_2. Pyromellitic dianhydride (PMDA) (**1a**) and 4,4′-oxydiphthalic anhydride (ODPA)

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doi:10.1016/j.polymer.2005.05.034

(**1b**) were purified by recrystallization from acetic anhydride and dried at 150 °C under vacuum before use. Other reagents and solvents were used as received.

2.2. Measurements

The infrared spectroscopy (IR) was taken with a Horiba FT-210 spectrophotometer. The ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker GPX300 (300 MHz) spectrometer. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed on a Seiko TG/DTA 6300 and DSC 6200, respectively. Refractive indices of PI films formed on quartz substrates were measured at a wavelength of 1.320 μm at room temperature with a Metricon model PC-2000 prism coupler. Using linearly polarized laser with parallel (TE: transverse electric) and perpendicular (TM: transverse magnetic) polarization to the film plane, the in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices and the film thickness of the samples were determined. The ε at 1.0 MHz frequency was calculated from the equation as follows: $\varepsilon = 1.10n_{\mathrm{AV}}^2$, where n_{AV} is average refractive index (i.e. $n_{\mathrm{AV}} = (2n_{\mathrm{TE}} + n_{\mathrm{TM}})/3$).

*2.3. Synthesis of 4-[2-(1-methoxy-2,6-dimethylphenyl)isopropylidene](2,6-dimethylphenol) (**2**)*

4,4′-Isopropylidenebis(2,6-dimethylphenol) (10.1 g, 35.6 mmol), iodomethane (2.21 ml, 35.6 mmol), potassium carbonate (10.3 g, 74.7 mmol), and acetone (100 ml) were refluxed for 24 h under nitrogen. After cooling this solution to room temperature, the reaction mixture was extracted with dichloromethane, and washed subsequently with 3 M aqueous NaOH solution to remove the starting material. The organic layer was evaporated, and the obtained solid was purified by silica gel column chromatography (toluene). The product was recrystallized from hexane to give a white-plate. The yield was 4.48 g (42%): mp 127–128 °C. IR (KBr): ν 3460 (Ar–OH), 2970, 2870 (C–H), 2827 (–OCH_3), 1600, 1489 (Ar), 1188 (C–O) cm^{-1}. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.84 (s, 2H), 6.82 (s, 2H), 4.48 (s, 1H), 3.70 (s, 3H), 2.23 (s, 3H), 2.20 (s, 3H), 1.59 (s, 3H). Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78. Found: C, 80.09; H, 8.53.

*2.4. Synthesis of 4,4′-bis{4-[2-(1-methoxy-2,6-dimethylphenyl)isopropylidene]-(2,6-dimethylphenyl)diphenyl ether (**3**)*

To the solution of compound **2** (5.74 g, 19.2 mmol) in quinoline (50 ml) and toluene (50 ml) was added potassium carbonate (3.32 g, 24.0 mmol), and the mixture was heated at 150 °C for 4 h to remove water with a Dean–Stark apparatus. After the formation of the potassium salt, toluene was removed by heating at 130 °C, and the solution was cooled to room temperature. To this suspension were added copper powder (0.122 g, 1.92 mmol) and 4-bromophenyl ether (3.15 g, 9.61 mmol), and the mixture was heated at 200 °C for 72 h under nitrogen atmosphere. After cooling the solution to room temperature, the reaction mixture was extracted with dichloromethane, and washed subsequently with 1 M aqueous HCl solution. The organic solvents were evaporated, and the residual oil was purified by silica gel column chromatography (toluene) to give oil. The yield was 1.90 g (26%). IR (KBr): ν 2966, 2870 (C–H), 2823 (–OCH_3), 1597, 1489 (Ar), 1196, 1176 (C–O–C) cm^{-1}. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.92 (s, 4H), 6.86 (s, 4H), 6.86 (d, $J = 8.4$ Hz, 4H, ArH), 6.69 (d, $J = 9.3$ Hz, 4H, ArH), 3.71 (s, 6H), 2.25 (s, 12H), 2.08 (s, 12H), 1.62 (s, 12H).

*2.5. Synthesis of 4,4′-{2-[oxybis(1-phenoxy-2,6-dimethylphenyl)isopropylidene](2,6-dimethylphenol)} (**4**)*

A solution of **3** (1.90 g, 2.49 mmol) in dry dichloromethane (15 ml) was cooled to −78 °C. BBr_3 (9.97 ml, 9.97 mmol in dichloromethane) was added and the reaction mixture was allowed to warm to room temperature for 2 h. The brown solution was cooled on ice and deionized water was slowly added. The organic layer was separated and the aqueous phase is extracted with 20 ml of dichloromethane twice. The combined organic layers were washed once with 50 ml of water, and dried with $MgSO_4$ and concentrated. The crude material was purified by silica gel column chromatography (dichloromethane/*n*-hexane = 4/1), to give a solid. The yield was 1.53 g (84%): mp 97–99 °C. IR (KBr): ν 3568 (Ar–OH), 2966, 2870 (C–H), 1604, 1489 (Ar), 1196, 1176 (C–O–C) cm^{-1}. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.92 (s, 4H), 6.85 (s, 4H), 6.86 (d, $J = 9.0$ Hz, 4H, ArH), 6.69 (d, $J = 9.0$ Hz, 4H, ArH), 4.50 (s, 2H), 2.22 (s, 12H), 2.07 (s, 12H), 1.62 (s, 12H). Anal. Calcd for $C_{50}H_{54}O_5$: C, 81.71; H, 7.41. Found: C, 81.42; H, 7.23.

*2.6. Synthesis of 4,4′-{{4-[2(4-nitrophenoxy)-2,6-dimethylphenyl]}isopropylidene}(2,6-dimethylphenoxy) diphenyl ether (**5**)*

A mixture of **4** (1.50 g, 2.04 mmol), 4-fluoro-1-nitrobenzene (0.47 ml, 4.47 mmol), potassium carbonate (0.618 g, 4.47 mmol), and dry DMF (30 ml) was refluxed for 14 h under nitrogen. The reaction mixture was allowed to cool to room temperature, and the mixture was then poured into water. The precipitate was collected by filtration and purified by silica gel chromatography (toluene) to give a solid. The yield was 1.80 g (yield 90%): mp 126–129 °C. IR (KBr): ν 2966, 2870 (C–H), 1589, 1489 (Ar), 1520, 1342 (NO_2), 1241, 1196, 1169 (C–O–C) cm^{-1}. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.22 (d, $J = 9.6$ Hz, 4H, ArH), 7.02 (s, 4H), 6.98 (s, 4H), 6.91 (d, $J = 8.7$ Hz, 4H, ArH), 6.89 (d, $J = 9.0$ Hz, 4H, ArH), 6.74 (d, $J = 9.0$ Hz, 4H, ArH), 2.14 (s, 12H), 2.10 (s, 12H), 1.71 (s, 12H). Anal. Calcd for $C_{62}H_{60}N_2O_9$: C, 76.21; H, 6.19; N, 2.87. Found: C, 75.66; H, 6.16; N, 3.00.