European Polymer Journal 45 (2009) 2348–2357

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Synthesis and characterization of poly(phenylene oxide) graft copolymers by atom transfer radical polymerizations

Mong Liang *, Yong-Jhao Jhuang, Chun-Fu Zhang, Wei-Jhuan Tsai, Hui-Chuan Feng

Department of Applied Chemistry, National Chia-Yi University, Chia-Yi 600, Taiwan

ARTICLE INFO

Article history:
Received 23 January 2009
Received in revised form 27 April 2009
Accepted 3 May 2009
Available online 12 May 2009

Keywords:
PPO-graft copolymer
Atom transfer radical polymerization (ATRP)
Couchman equation
Compatible

ABSTRACT

A series of comb-like poly(phenylene oxide)s (PPO) graft copolymers with controlled grafting density and length of grafts were synthesized by atom transfer radical polymerization (ATRP). The α-bromo-poly(2,6-dimethyl-1,4-phenylene oxide)s (BPPO) were used as macroinitiators to polymerize vinyl monomers and the graft copolymers carrying polystyrene (PS), poly(*p*-acetoxystyrene) (PAS), and poly(methyl methacrylate) (PMMA) as side chains were synthesized and characterized by NMR, FTIR, GPC, DSC and TGA. The composition-dependent glass-transition temperatures (T_g) of PPO-*g*-PS exhibited good correlation with theoretical curve in Couchman equations except for the cases of low PS content (<40 mol%) copolymers in which a positive deviation was observed due to enhanced molecular interactions. The increase in monomer/initiator ratio led to the increase of degree of polymerization and the decrease of polydispersity. Despite the immiscibility nature between PPO and PMMA, the PPO-*g*-PMMA exhibited enhanced compatibilization as apparent single T_g in a wide temperature window throughout various compositions revealing an efficient segmental mixing on a molecular scale due to grafting structure.

1. Introduction

Recently, preparation of new graft copolymers have attracted considerable attention as their potential use in membrane separation technology, modification of conducting polymers [1], surface modification [2,3], and brush-type copolymers [4,5]. Through proper design or modifications, new polymeric structures with tailor-made properties are accessible for different applications. For the past decades, various grafting techniques including chemical, radiation, photochemical, plasma-induced and enzymatic have been developed to design new materials with optimal thermo, physical, mechanical and optical properties. Among them, atom transfer radical polymerization (ATRP) is one of the successful and convenient methods for new graft polymer synthesis because it can be carried out under relatively mild conditions and allows a variety of vinyl monomers to be polymerized in a controlled fashion with well-defined structures. So far three types of grafting methods employing ATRP have been used, which are grafting-through [6], grafting-to [7–9] and grafting-from [10–12], concerning the synthesis and application of graft copolymers. The grafting-from technique which involves the preparation of a multi-functional macroinitiator with a predetermined number of pendent reactive sites on polymer backbone has been widely used for molecular brushes synthesis due to its controllable grafting density, and adjustable amphiphilicity [13–15]. Despite the extensive effort in grafting-from method, most of the resulting copolymers consist of ethylene structure as backbone, whereas few of non-ethylene main chain skeletons such as cellulose [16,17], vinyl chloride [18] and vinylidene fluoride [19,20] were also reported. Styrene, acrylate and methacrylate are most commonly used monomers to graft onto various polymer backbones [14,21–23] to modify

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* Corresponding author. Address: Department of Applied Chemistry, National Chia-Yi University, 300 University Rd., Chia-Yi 600, Taiwan. Tel.: +886 5 2717952; fax: +886 5 2717901.
E-mail address: mliang@mail.ncyu.edu.tw (M. Liang).

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doi:10.1016/j.eurpolymj.2009.05.008

their surface properties and compatibility; however, the weak thermal stability largely limited the usage in high performance applications due to the inherent flexible backbone nature. Although recent progress in surface-initiated ATRP have shown examples in grafting PET [24], PC [25] and nylon [26] membrane surfaces with *N*-isopropyl acryl amide and 2-hydroxyethyl methacrylate in a heterogeneous fashion, little work has been conducted homogeneously with better thermal stability, solubility and processibility of the resulting copolymers, and to the best of our knowledge, reports regarding the synthesis and thermal properties of polyphenylene oxide (PPO) graft copolymers have yet to be explored. This is probably due to the poor solubility of the engineering plastics in common organic solvents and the difficulty in obtaining a complete initiation process on the backbone with a well-characterized architecture. In the present study, we report the use of grafting-from method to synthesize a series of comb-like PPO-graft copolymers and terpolymers carrying polystyrene (PS), poly-4-acetoxystyrene (PAS) and poly(methyl methacrylate) (PMMA) as side chains, starting from well-defined α-brominated poly(phenylene oxide) (BPPO) macroinitiators obtained in our previous work [27].

Poly(phenylene oxide) (PPO) is a well-known engineering plastic with a low dielectric constant of 2.58 (at 23 °C 60 Hz) and a high glass transition temperature (T_g) of approximately 212 °C. It is one of the potential materials to satisfy the demand of high frequency substrates in the electronics industry and its alloys are widely used in electrical appliance due to the balanced physical, chemical and electrical properties. PPO has been blended with various materials to improve its brittleness and processibility, however, except for PPO/PS system, most blends are immiscible because of their unfavorable intermolecular interactions which, in turn, attribute to the deterioration in mechanical properties at phase boundaries. Much of the work is concerned with the enhancement of interfacial adhesion between phases by incorporating the compatibilizers, nevertheless, the decrement of glass transition temperature or thermal decomposition temperature arising from the low molecular weight compatibilizers are common drawbacks of the polymer blends. The key aspect of this study was to graft polymer from PPO with different miscibility segments using ATRP method and investigated their compatibility and thermal properties.

2. Experimental

2.1. Materials

All reagents and solvents were reagent-grade. Poly(2,6-dimethyl-1,4-phenylene oxide) of intrinsic viscosity equal to 0.4×10^{-3} m^3 kg^{-1} (i.e., 0.4 dL g^{-1}) in chloroform at 25 °C was obtained from General Electric Plastics and purified by precipitation from chloroform solution into methanol before use. *N*-Bromosuccinimide (NBS; Acros), 2,2′-Azobis-isobutyronitrile (AIBN; Showa), 2,2′-bipyridine (Bpy; Acros), Copper chloride (CuCl; Showa) were purchased from commercial sources and used as received without purification. Chlorobenzene, chloroform, *n*-hexane (all from TEDIA), methyl alcohol (from Mallinckrodt) were purchased from commercial companies and used as received. Styrene (Sty; Acros) and *p*-acetoxystyrene (PAS; TCI) were washed twice with 5% NaOH solution and then water, which was subsequently dried over anhydrous magnesium sulfate ($MgSO_4$; J.T. Baker) and distilled under reduced pressure. Methyl methacrylate (MMA; Fluka) was freshly distilled before polymerization. Toluene (Tedia) was refluxed with calcium hydride (CaH_2; Fluka) and then distilled under nitrogen.

2.2. Instrumentation

^{1}H and ^{13}C NMR spectra were recorded on a 300 and 75 MHz Varian – Mercury$^+$ 300 spectrometer, respectively, using the $CDCl_3$ solvent and the internal standard tetramethylsilane. Fourier transform infrared spectroscopy (FTIR) spectra were recorded for KBr disks using a Shimadzu FT-IR 8400 spectrometer. The molecular weight of the polymers was determined by gel permeation chromatography (GPC) which was carried out with polymer solutions in THF. Samples were prepared at nominally 1 mg mL^{-1} in THF and filtered through a 0.45 μm syringe filter and injected by WATERS717 Autosample. GPC system (Waters 515 HPLC pump, 1 mL/min, 40 °C) were equipped with WATERS STYRAGEL HR0.5, HR4E, HR5 and a Waters refractive index detector (Model 2410). DSC measurements were performed on a DSC Q10 Differential Scanning Calorimeter (TA Instrument). Samples of about 5 mg were weighed and hermetically sealed into aluminum pans (diameter: 5 mm, TA Instruments) for standard DSC analysis. The glass-transition temperatures of the PPO-*g*-PS and PPO-*g*-PAS were determined by heating at a rate of 20 °C/min to 280 °C, held there for 10 min and then cooled to 40 °C in fast equilibrium to obtain amorphous state samples, then repeated the program at a rate of 20 °C/min again. For PPO-*g*-PMMA, the samples were treated similarly except the temperature was heated up to only 250 °C. All the T_g values were measured after the 2nd heating scan. The nitrogen gas flow was 50 mL/min. Thermogravimetric analysis was performed with a TGA Q50 (TA instrument) thermogravimetric analyzer under nitrogen atmosphere. Heating scans carried out from 30 to 800 °C at 20 °C/min.

2.3. Synthesis of macroinitiator poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO)

To a stirred solution of 2.4 g PPO in chlorobenzene (100 mL) was added *N*-bromosuccinimide (0.89 g, 5 mmol), and 2,2′-azobis-isobutyronitrile (0.1 g, 0.6 mmol). The mixture was irradiated with mercury lamp (100 W) placed at a short distance (2 in., 21700 μW/cm^2) from reaction vessel and heated at reflux conditions for 3 h. After cooling, the reaction mixture was added to a 10-fold excess of *n*-hexane to precipitate the product. The polymer was filtered and washed with methanol, which was redissolved in minimum amount of chloroform and precipitated into a 10-fold excess of methanol solution. The polymer was collected as a light yellow powder and dried under vacuum for overnight (BPPO(L), bromination ratio: 10%). By the same procedure,