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Synthesis, thermal properties, and specific interactions of high T_g increase in poly(2,6-dimethyl-1,4-phenylene oxide)-*block*-polystyrene copolymers

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Abstract

We have synthesized a series of block copolymers of poly(2,6-dimethyl-1,4-phenylene oxide) and polystyrene (PPO-*b*-PS copolymer) by atom transfer radical polymerization. The PS content in these copolymer systems was determined by using infrared spectroscopy, thermal gravimetric analysis, and solution and solid-state NMR spectroscopy; good correlations exist between these characterization methods. DSC analyses indicated that the PPO-*b*-PS copolymers have higher glass transition temperatures than do their corresponding PPO/PS blends. Our FTIR and solid-state NMR spectroscopic analyses suggest that the PPO-*b*-PS copolymers possess stronger specific interactions that are responsible for the observed relatively higher values of T_g. We found one single dynamic relaxation from the dynamic mechanical analysis, which implies dynamic homogeneity exists in the PPO-*b*-PS copolymer; this result is consistent with the one single proton spin–lattice relaxation time observed in the rotating frame [$T_{1\rho}$(H)] during solid state NMR spectroscopic analysis. In addition, the 2D FTIR spectroscopy reveals evidence for the stronger interactions between segments of PPO and PS through the formation of π-cation complexes.

Keywords: ATRP; Block copolymer; Specific interactions

1. Introduction

Miscible polymer blends provide a cost-effective method for developing new materials in polymer science industries by avoiding the need to develop new polymers. For example, the well known poly(2,6-dimethyl-1,4-phenylene oxide)/polystyrene (PPO/PS) miscible blend system has widespread commercial use in the thermoplastics industry [1–3]. The glass transition temperature (T_g) of a polymer is an important intrinsic characteristic that influences its material properties and potential applications. Furthermore, polymers having high values of T_g are attractive for industrial applications because of strong economic rewards. It is well known that the dependence of the value of T_g on the composition of miscible PPO/PS blends obeys the Fox rule. In a previous study [4], we found that the values of T_g of poly(vinylphenol)/poly(vinylpyrrolidone) (PVPh/PVP) blends are substantially higher than the values predicted by the Fox rule, and that this phenomenon is due to the presence of hydrogen bonding interactions. Furthermore, DSC, FTIR and solid state NMR spectroscopic analyses suggest that the values of T_g and the strength of hydrogen bonding of PVPh-*co*-PVP copolymers are both greater than those of their corresponding PVPh/PVP blends at the same mole fractions of PVPh [5,6]. Therefore, in an attempt to raise the value of T_g of the miscible PPO/PS blend, in this study we synthesized the PPO-*b*-PS copolymer.

The desire to control polymer properties through the synthesis of block copolymers and complex macromolecular architectures is a continuing theme throughout polymer chemistry [7,8]. Block copolymers are remarkable self-assembling systems that can assume a wide variety of morphologies, including lamellar, hexagonal-packed cylindrical, and body-centered cubic micellar structures, as a result of the presence of two immiscible polymer chains connected by covalent bonds and depending on the relative

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volume fractions of the blocks [9–12]. The block copolymers that have well defined structures, such as known molecular weights, molecular weight distributions, compositions, architectures, and end group functionalities, are in high demand. Such block copolymers have been synthesized in three ways [13]: (1) Sequential monomer addition, (2) coupling reactions of ‘living’ polymer chains, and (3) mechanism transformation. The development of ionic polymerization methods has allowed the preparation of copolymers with controlled chain-end functionalities and well-defined blocks and grafts [14–17]. These polymerizations, however, must be undertaken with nearly complete exclusion of moisture and often at very low temperatures. Moreover, only a few types monomers can be polymerized through these routes, and the use of more-functionalized monomers may cause undesired side reactions to occur. Recently, Matyjaszewski and Sawamoto [18] et al. have reported that atom transfer radical polymerization (ATRP) allows the synthesis of polymers that have narrow molecular weight distributions [19] and of well defined block copolymers [20,21] and star polymers [22,23]. ATRP has gained tremendous interest lately because it is tolerant of impurities, adventitious water, and high temperatures. The ATRP process uses an alkyl halide as initiator, a metal in its lower oxidation state, and complexing ligands [24–31]. The process involves the successive transfer of the halide from the dormant polymer chain to the ligated metal complex, thus establishing a dynamic equilibrium between the active and dormant species. This controlled radical polymerization allows the polymerization of a wide range of monomers, such as styrenes, acrylates, and methacrylates, as well as a variety of functional monomers.

In the literature, block copolymers having self-regular morphologies have emerged primarily from the investigation of diblock copolymers whose macrophase or microphase separation has been studied as a function of their compositions and interaction parameters. In contrast, we intended to synthesize PPO-*b*-PS block copolymers through ATRP, even though the PPO and PS units are well-known to form a miscible blend system [32–34]. Our approach was to modify the hydroxyl end group of PPO to form an α-haloester, which is one type of potential initiator for atom transfer radical polymerization.

FTIR and NMR spectroscopies are powerful tools for characterizing the detailed structures of polymers and their specific interactions because these features affect local electron densities so that corresponding frequency shifts can be observed [35–38]. Moreover, the phase behavior and molecular mobility of polymer blends or copolymers can be estimated from the proton spin–lattice relaxation time in the rotating frame $\left(T_{1\rho}^{\mathrm{H}}\right)$ measured by solid state NMR. The nature of the specific interactions in PPO/PS blends has been studied extensively. Based on solution NMR and X-ray photoelectron spectroscopic studies, Porter, Wang, and Goh have concluded that intermolecular interactions in PPO/PS blends exist between the methyl groups of PPO and the phenyl rings of PS [39–41]. In addition, proton spin diffusion experiments have indicated that PPO and PS units mix at a molecular level [42]. Recently, generalized two-dimensional (2D) correlation spectroscopy has been applied widely in polymer science [43]. This novel method can allow the specific interactions between polymer chains to be investigated by treating the spectral fluctuations as a function of time, temperature, pressure, and composition. Two-dimensional IR correlation spectroscopy can identify different intra- and intermolecular interactions through the analysis of selected bands from the 1D vibration spectrum. Noda [44] and Painter [45] have reported the 2D correlation IR spectra of PPO/PS blends. Noda’s results suggest that the methyl groups of PPO segments in PPO/PS blends play an important role, but Painter’s analysis of the same system concluded that the specific interaction between the PPO and PS chains probably is due to the formation of π-cation complexes [46,47] between the methyl groups of PPO and the aromatic rings of PS.

In this study, we have synthesized a series of block copolymers containing various PPO and PS contents to compare their glass transition temperatures with those of the corresponding PPO/PS blends. We have observed a significant glass transition temperature increase, relative to those of PPO/PS blends, by thermal analyses and have investigated the specific interactions present in these PPO-*b*-PS copolymers by using solid state NMR and 2D FTIR spectroscopies.

2. Experimental

2.1. Materials

Styrene was distilled from calcium hydride before use. Monomers were stored in a freezer. Copper (I) bromide (CuBr) was stirred in glacial acetic acid overnight, filtered, and then rinsed with absolute ethanol under a blanket of argon and dried under vacuum at 80 °C for 3 days. Toluene, THF, pyridine, and acetonitrile were distilled prior to use. *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) was used as received. PPO was purchased from GE Company (BLENDEX® HPP857).

2.2. Preparation of PPO/PS blends

Desired composition of PPO (BLENDEX® HPP857) and commercial PS ($M_n = 45{,}000$ g/mole, $T_g = 100$ °C) was dissolved in toluene at a concentration of 5 wt% and stirred for 6–8 h. These solutions were allowed to evaporate slowly at 50 °C for 1 day on a teflon plate and dried at 90 °C for 1 day to ensure total elimination of the solvent, and then further dried under vacuum at 90 °C for 2 days.