Synthesis and characterization of phosphonated Poly(ethylene terephthalate) ionomers

Lin Ju [a, c], Juan Pretelt [b, c], Tianran Chen [b, c], Joseph M. Dennis [a, c], Katherine V. Heifferon [a, c], Donald G. Baird [b, c], Timothy E. Long [a, c], Robert B. Moore [a, c, *]

[a] Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA, 24061, United States
[b] Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA, 24060, United States
[c] Macromolecules Innovation Institute, Virginia Polytechnic Institute and State University, Blacksburg, VA, 24061, United States

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ABSTRACT

A more efficient route for the synthesis of phosphonated dimethyl isophthalate, disodium salt is shown to provide a significantly higher yield (42%), in contrast to a previously reported yield (15%). This higher yield enabled the synthesis of phosphonated poly(ethylene terephthalate) (PPET) ionomers using conventional melt polycondensation with ethylene glycol and dimethyl terephthalate. The physical properties of these phosphonated PET ionomers (Na$^+$-PPET) were characterized using differential scanning calorimetry (DSC), melt rheology, and tensile testing. DSC analysis showed that the crystalline melting temperatures, crystallization temperatures, degrees of crystallinity, and crystallization rates decreased with increasing ionic content. Melt rheology confirmed the existence of physical crosslinks in Na$^+$-PPET ionomers, as indicated by a crossover of the storage and loss moduli, attributed to strong electrostatic associations between phosphonated units on the polymer chains. Tensile tests of the Na$^+$-PPET samples showed enhanced Young's modulus and yield stress compared to pure PET.

1. Introduction

Ionomers are charged polymers containing minor amounts of covalently attached ionic functionalities, typically less than 15 mol %, incorporated into or pendant to the polymer backbones [1–3]. Generally, the polar ionic groups, surrounded by a less polar matrix, tend to form nanometer-sized ionic aggregates due to attractive Coulombic interactions between the ionic-pairs [4]. These ionic aggregates, acting as physical crosslinks, decrease the mobility of polymer chains, and are known to exert a profound effect on the thermo-mechanical and rheological properties of polymers [5–7]. Compared to nonionic analogues, semi-crystalline ionomers have been shown to exhibit a higher modulus, higher melt viscosity, and a significant decrease in the overall rate of crystallization [8–10]. The ability to control thermo-mechanical and rheological properties by choice of ion type and content provides the opportunity for ionomers to be applied in a wide variety of technologies, such as coatings [11,12], adhesives [13,14], dyeable textile materials [15,16],

polymer blend and nanocomposite compatibilization [17,18], shape memory polymers [19,20], and self-healing materials [21,22].

The valence of charged monomer units in ionomers can vary with the type of ionic species attached to the ionomer chains and the type of neutralizing counterions. For the purposes of the following discussion, the ionic groups that are covalently attached to the ionomer backbone will be referred to as *pendant ions*, whereas the free ions that electrostatically neutralize the pendant ions will be referred to as *counterions*. Ionomers containing anionic pendant ions are usually called *anionic ionomers*, while those bearing cationic pendant ions are named *cationic ionomers*. A relatively wide range of both monovalent (e.g., carboxylates, sulfonates) and multivalent (e.g., phosphonates, dicarboxylates) pendant anions have been utilized for the preparation of anionic ionomers [23–28]. Both monovalent counterions (e.g., the alkali metal ions, organic alkyl ammonium ions (e.g., ammonium, pyridiniums) and multivalent counterions (e.g., the alkaline earth ions, transition metal ions) can be used to neutralize anionic pendant ions. Cationic ionomers containing monovalent (e.g., quaternary ammoniums, pyridiniums, imidizoliums) and multivalent pendant cations (e.g., 1,4-diazabicyclo[2.2.2]octane (DABCO) double ammoniums salt) have also been described in the literature [29–31].

* Corresponding author. Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA, 24061, United States.
  E-mail address: rbmoore3@vt.edu (R.B. Moore).

Monovalent anions (e.g., the halides, tosylate anions) have been utilized to neutralize these pendant cations.

Ionomers bearing multivalent counterions have attracted significant attention because they offer a greater range of Coulombic interactions, and thus physical properties, as compared to ionomers containing both monovalent pendant ions and counterions [32—38]. Typically, monovalent pendant ions are used to coordinate with only monovalent counterions to generate a physical crosslink *via* an dipole-dipole interactions between two or more ion pairs. In contrast, multivalent counterions can form an ionic bond between two monovalent pendant anions, which establishes a fundamentally stronger physical crosslink in satisfying the requirement for local charge neutrality [37]. For example, compared to sulfonated poly(ethylene terephthalate) (SPET) ionomers containing monovalent counterions (Na^+, and Li^+), SPET ionomers with divalent counterions, such as alkaline earth (Ca^{2+}) and divalent transition metal cations (Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}), display longer crystallization half times due to restricted mobility of the polymer chains. In addition, SPET/poly(ethyl acrylate-*co*-4-vinylpyridine) (EAVP) blends containing divalent counterion exhibit enhanced modulus and tensile strength [32—35]. However, aside from the widely applied Surlyn® ionomers, few other ionomers with multivalent counterions are commercially applicable due to the difficulty of conversion to multivalent counterions by neutralization of the acid groups or by ion exchange of monovalent counterions [39,40].

Recently, ionomers containing multivalent pendant ions have emerged as interesting candidates for the design of new ionomers with enhanced properties governed by multivalency. The multivalent pendant ion generates multiple dipole-diploe interactions per functional group between two ion pairs that provides a stronger physical crosslink due to the increased charge density compared to monovalent analogues. Direct polymerization of ionic monomers bearing multivalent pendant ions generally provides better tunability regarding ion type, concentration, and distribution within the polymer chain. However, only a few reports describe ionic monomers that contain multivalent pendant ions. Kim et al. [27] synthesized poly(styrene-*co*-itaconate) ionomers that have two ion pairs in the same ionic repeat unit, and found that the cluster T_g of the itaconate ionomers is much higher than that of monovalent methacrylate ionomers. Zhang et al. [31] synthesized a cationic ionomer containing the divalent 1,4-diazabicyclo[2.2.2]octane (DABCO) salt, which displays superior thermomechanical properties and promotes more well-defined microphase-separation compared to analogous ionomers bearing singly-charged pendant groups. Other reports of polymers containing multivalent pendant groups have focused on the acid form of phosphonated polymers (e.g., polysulfone, poly(ether ether ketone)) or phosphonated polyelectrolytes (e.g., phosphonated poly(*m*-phenylene)) [41—43]. Little information exists, however, regarding the properties of ionomers bearing multivalent pendant ions with monovalent counterions.

Sulfonated poly(ethylene terephthalate) ionomers in Na^+-form (Na^+-SPET) are one of the most widely studied polyester ionomers, and was originally commercialized by DuPont as textile fibers with improved dyeability to basic dyes compared to pure PET [44,45]. While the introduction of sulfonate groups onto PET has been shown to enhance mechanical properties, the strong ionic interactions are also known to slow the rate of crystallization and adversely affect processability due to a high melt viscosity [46—49]. Due to the advantage of specific interactions of sulfonate groups with a wide range of polar materials, SPET ionomers are often applied in compatibilizing polyester/polyamide blends by generating attractive interactions between the sulfonate salt functionalities and the amide units of the polyamide. In these inherently immiscible blends, the specific interactions lower the interfacial tension leading to a reduction in phase dimensions [50—54].

Despite the well-studied effect of monovalent sulfonate pendant ions on the properties of SPET ionomers, no systematic studies have been focused on the investigation of PET ionomers bearing multivalent pendant ions, such as phosphonate salts. To date, only one patent reference of limited scope from 1962 refers to a phosphonated PET ionomer in Na^+-form (Na^+-PPET) [55]. This patent described that melt polycondensation with ethylene glycol, dimethyl terephthalate, and the phosphonate ionic monomer yielded Na^+-PPET ionomers that could be processed into textile fibers with an affinity for basic type dyes, such as colored cationic organic substances containing sulfonium, oxonium, or quaternary ammonium functional groups. No other detail regarding thermal, rheological, or mechanical properties of the resulting Na^+-PPET ionomers were reported. Nevertheless, the yield of the essential phosphonated isophthalate monomer was reported to be only 15%, which apparently limited subsequent comprehensive structure-property investigations. Moreover, the Na^+-PPET ionomers synthesized in this patent exhibited substantial insolubility in solvents commonly used to dissolve linear polyesters, but they remained melt-processable. Not surprisingly, this very low yield limited industrial applicability of Na^+-PPET ionomer, and no further reports of PPET have surfaced.

To expand our fundamental understanding of PET-based ionomers, this work focuses on an improved synthetic route for Na^+-PPET ionomers and a detailed characterization regarding their thermal, mechanical, and rheological properties. With a substantially modified synthetic scheme that achieves a significantly higher yield of the phosphonated monomer, we have generated PPET with various ionic contents to probe the effects of multivalent pendant ions on the physical properties of this potentially valuable class of polyester ionomers. Physical characterization, including thermal, rheological, and mechanical analyses, are correlated to establish valuable structure-property relationships for these PET ionomers containing pendant phosphonate groups.

2. Experimental section

Materials. All reagents were used as received without further purification. Dimethyl 5-aminoisophthalate (DMAIP, 98%), sodium nitrite ($NaNO_2$, ≥97.0%), sodium tetrafluoroborate ($NaBF_4$, 98%), copper(I) bromide (CuBr, 98%), phosphorus trichloride (PCl_3, 99%), sodium methoxide (NaOMe, 95%), sodium hydroxide (NaOH, ≥98%), Chelex® 100 sodium form (50—100 mesh), dimethyl terephthalate (DMT, ≥99%), ethylene glycol (EG, anhydrous, 99.8%), sodium acetate (NaOAc, >99%, anhydrous), manganese(II) acetate tetrahydrate ($Mn(OAc)_2 • 4H_2O$, 99.99%), and *n*-butanol (99%) were purchased from Sigma-Aldrich. $Ti(OiPr)_4$ was diluted to 10.18 mg/mL in *n*-butanol, and $Mn(OAc)_2 • 4H_2O$ was diluted to 21.5 mg/mL in ethylene glycol. All deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc.

Synthesis of Dimethyl 5-Phosphoisophthalate Disodium Salt. Dimethyl 5-phosphoisophthalate disodium salt was synthesized following a four step procedure, as shown in Scheme 1. In the first step, dimethyl 5-aminoisophthalate (10.0 g, 47.9 mmol), sodium tetrafluoroborate (8.94 g, 81.4 mmol), hydrochloric acid (11.65 M, 6.7 mL), and distilled water (19.0 mL) were added to a 250-mL, round-bottomed flask equipped with a magnetic stir bar. The flask was placed into an ice bath with constant stirring. A saturated sodium nitrite (3.3 g, 47.9 mmol) solution in H_2O was then added into the mixture dropwise, and allowed to stir for 1 h. A yellow precipitate was formed and removed from the solution using vacuum filtration. The precipitate was washed with cold saturated sodium tetrafluoroborate solution (2×5 mL) and cold diethyl ether