4584 *Macromolecules* **2010**, *43*, 4584–4588
DOI: 10.1021/ma100458v

Macromolecules
ARTICLE

Quantitative Poly(vinyl alcohol) Modification in Ionic Liquids: Esterification and Urethanation with Low Surface Tension Producing Reagents

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Received February 26, 2010; Revised Manuscript Received April 14, 2010

ABSTRACT: A method for rapid and quantitative chemical modification of poly(vinyl alcohol) (PVOH) is described using two different ionic liquids as reaction solvents. The quantitative modification of alcohol-containing polymers such as PVOH, cellulose, and other polysaccharides has been elusive due to solvent incompatibility with respect to alcohol-reactive reagents and to the limited solvent options for these polymers. Ionic liquids are ideally suited to address this problem as they are a diverse and extremely tunable class of solvents. Two ionic liquids that differ in both their cation and anion are demonstrated to dissolve and facilitate quantitative modification of PVOH under simple reaction conditions. Rapid esterification of PVOH using four different acid chlorides is demonstrated in both 1-butyl-3-methylimidazolium chloride (BMIM-Cl) and tri-*n*-butylethylphosphonium diethylphosphate (TBEP-DEP). Urethanation of PVOH was also demonstrated to be quantitative with the appropriate ionic liquid solvent. The reagents chosen for the modification of PVOH were selected based on their low surface tension. Controlling ionic liquid surface properties by the adsorption of partially modified PVOH to the ionic liquid/air interface was an initial objective. The surface tension and surface chemical composition of modified polymer/ionic liquid solutions demonstrate that polymer adsorption to the liquid/vapor interface occurs and that this is more prominent with increasing extent of PVOH modification.

Introduction

The modification of polymers that contain alcohol functionality, such as cellulose and poly(vinyl alcohol) (PVOH), has been of great interest for many years and has resulted in products ranging from guncotton to tissue scaffolds.[1−7] Current modification methodologies for these polymers, however, remain complex and time-consuming despite the long-tenure interest in this area of research. For PVOH specifically, esterification[8−12] and urethanation[13] have been demonstrated; however, slow reaction kinetics and nonquantitative reaction yields are reported. These reaction limitations are due to the limited number of solvents that dissolve PVOH and do not interfere with alcohol chemistry. Significant efforts have been made to find alternative solvents for PVOH[14] that can facilitate rapid, quantitative modification of this polymer under simple reaction conditions. *N*-Methylpyrolidone may be sufficient for certain modifications,[12] but in other cases, designer solvents such as cyclic ureas are required to be synthesized to study potential solvent alternatives.[9] In all cases, however, the modification of PVOH is a time-intensive and nonquantitative process.

Ionic liquids are ideally suited as alternative solvents for polymer modification and therefore can address some of the complications associated with the quantitative modification of alcohol functionality on polymers including PVOH and polysaccharides. These neoteric solvents possess several advantages over traditional organic solvents including negligible vapor pressure and high charge density.[15,16] Ionic liquid solvents are highly tunable as changing the cation/anion pair can adjust the melting point, viscosity, solvating power, and hydrophobicity/hydrophilicity, making this class of solvents extremely versatile for numerous processes.[15,17−20]

While there has been minimal effort in the area of polymer solubility in ionic liquids,[21,22] a notable discovery[18] by Swatloski and Rogers is that cellulose dissolves readily in imidazolium chloride ionic liquids. These ionic liquids disrupt hydrogen bonding and allow for the dissolution of cellulose. This natural polymer is virtually insoluble in water and other common organic solvents. These same imidazolium chloride ionic liquids are likely candidates for dissolution of similar polymer systems; thus, we have applied them to poly(vinyl alcohol), a semicrystalline polymer with similar solubility complications. We have used two ionic liquids, 1-butyl-3-methylimidazolium chloride (BMIM-Cl) and tri-*n*-butylethylphosphonium diethylphosphate (TBEP-DEP), to demonstrate dissolution and subsequent modification of PVOH. Both ionic liquids contain anions which should hydrogen bond with the polymer hydroxyl groups and aid in the dissolution of the polymer.[18,23] Chemical moieties with low surface energies were chosen for the polymer modifications in order to direct the modified polymer to the ionic liquid/air interface and tune the solution surface tension and surface chemical composition. These studies may have important implications for PVOH electrospinning and other processes where surface and interfacial properties are paramount.[24,25]

Experimental Section

Materials. Poly(vinyl alcohol) (99+% hydrolyzed, 89 000−98 000 MW), acetyl chloride, octanoyl chloride, heptafluorobutyryl chloride, pentadecafluorooctanoyl chloride, octyl isocyanate, dibutyltin dilaurate, and anhydrous pyridine were purchased from Aldrich and used as received. 1-Butyl-3-methylimidazolium

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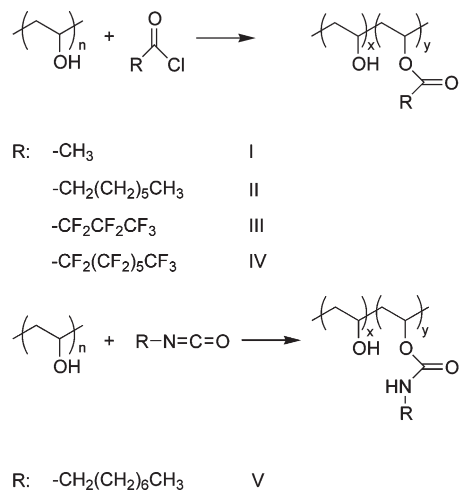

Figure 1. Esterifications and urethanation carried out on PVOH in ionic liquids.

chloride (BMIM-Cl) was purchased from Fluka Chemical Co., dried at reduced pressure and 80 °C for 48 h, and stored in a sealed round-bottom flask under a positive pressure of dry nitrogen until needed. Tri-*n*-butylethylphosphonium diethylphosphate (TBEP-DEP) was donated by Cytec and purified as per the procedures for BMIM-Cl.

Preparation of Poly(vinyl alcohol)/Ionic Liquid Solutions. Solid PVOH (1.0 wt %) was added to 20 mL scintillation vials containing ionic liquid and a magnetic stir bar. The vials were capped with rubber septa and purged with dry nitrogen throughout the polymer dissolution process to remove any residual water from the polymer/ionic liquid solution. The mixture was allowed to stir at 90 °C for 18−48 h or until the PVOH was fully dissolved. It is important to note that 1.0 wt % PVOH solutions were used in order to minimize solution viscosity, and it is not the limit for polymer solubility in the ionic liquids. Solutions as high as 10.0 wt % PVOH in both BMIM-Cl and TBEP-DEP have been prepared and determined to be completely miscible by visual inspection. These solutions are extremely viscous, making it difficult to perform dynamic light scattering measurements or modifications via magnetic stirring at the temperatures defined subsequently. Higher concentrations than 10.0 wt % PVOH in BMIM-Cl and TBEP-DEP may be accessible using the dissolution techniques demonstrated for cellulose by Swatloski et al.[18]

The prepared PVOH solutions were used immediately after the polymer was completely dissolved to avoid absorption of water into the solution. Dynamic light scattering was carried out on each polymer/ionic liquid solution as well as a 1 wt % water/PVOH solution to confirm the dissolution of PVOH in the respective solvent (see Supporting Information Figures S1−S4). Hydrodynamic radii of 10.9 and 5.5 nm were measured for 1 wt % PVOH/water solutions and 1 wt % TBEP-DEP solutions, respectively. Light scattering experiments for PVOH/BMIM-Cl solution were inconclusive as the solutions fluoresce under the incident beam. Visual transparency and increased solution viscosity, however, imply that the PVOH is dissolved in BMIM-Cl (see the Supporting Information for further details).

Esterification of Poly(vinyl alcohol) in Ionic Liquid Solvents. Esterification of PVOH was carried out using four different acid chlorides (Figure 1). A particular fraction of the stoichiometric amount (relative to hydroxyl groups) of the acid chloride was introduced to a PVOH/ionic liquid solution to obtain a specified extent of polymer modification. All reactions were carried out at 90 °C with constant stirring unless otherwise specified. The only difference in the reaction conditions for the different ionic liquid solutions was the time allotted for the reactions to take place. PVOH/TBEP-DEP solutions were allowed to react for 1 h, whereas PVOH/BMIM-Cl solutions were allowed to react for 10−15 min as the reactions were found to reach full conversion in these allotted times. Reactions were carried out both with and without pyridine, a typical esterification catalyst and acid scavenger, and it was determined that addition of catalyst did not affect the reaction kinetics. The resulting polymer products were precipitated from the ionic liquid with a nonsolvent which varied depending on the extent of modification. Water was used to precipitate PVOH modified above 50%, while chloroform was used for PVOH modified below 50%. The precipitate was isolated by centrifugation and washed three times with an appropriate nonsolvent to remove residual ionic liquid. The polymer was then dried at reduced pressure and 60 °C and stored in sealed scintillation vials.

Urethanation of Poly(vinyl alcohol) in Ionic Liquid Solvents. Urethanation of PVOH was carried out using octyl isocyanate in a manner similar to the esterification reactions mentioned previously (Figure 1). A particular fraction of the stoichiometric amount of octyl isocyanate was introduced into the PVOH/ionic liquid solutions to obtain the desired extent of polymer modification. These reactions were carried out both with and without dibutyltin dilaurate, a typical urethanation catalyst. All reactions were carried out at 90 °C with constant stirring and were allowed to react for 18−24 h. Polymer isolation and purification methods were identical to those described for the synthesis of the polyesters mentioned previously.

Characterization of Isolated, Modified PVOH. All isolated polymer products were analyzed by attenuated total reflectance infrared (ATR-IR) spectroscopy using a HORIBA Jobin Yvon HR800 spectrometer equipped with an ATR-IR lens and X-ray photoelectron spectroscopy (XPS) using a Quantum 2000 scanning ESCA microprobe (Physical Electronics). 100% modified, unfluorinated polymers were found to redissolve in chloroform and were analyzed by nuclear magnetic resonance spectroscopy (NMR) using a Bruker-Spectrospin 300 Hz nuclear magnetic resonance spectrometer. All other polymer products were insoluble in typical NMR solvents.

Preparation of Modified Polymer/Ionic Liqud Solutions for Surface Characterization. Partially modified PVOH/ionic liquid solutions were prepared in the same manner as described previously, except that the polymer was not isolated. Instead, the polymer was left in solution, and the entire solution was dried under reduced pressure at 60 °C for 18 h. These solutions were then sealed under dry nitrogen until surface characterization experiments were carried out.

Surface Characterization of Ionic Liquids and Polymer/Ionic Liquid Solutions. The surface activity of partially modified PVOH was analyzed by studying the surface tension and surface chemical composition of all polymer/ionic liquid solutions as a function of extent of polymer modification. The chemical compositions of all ionic liquids and polymer/ionic liquid solutions were determined by X-ray photoelectron spectroscopy analysis. Surface tension was determined by the Wilhelmy plate method using a Langmuir−Blodgett tensiometer equipped with a microbalance and a cylindrical steel probe. The tensiometer was calibrated by taring the microbalance with the probe suspended in air and subsequently placing the probe in deionized water to measure the tensile force on the probe. This force was calibrated to a surface tension of 72.8 dyn/cm. The probe was then moved to the desired solution, and the surface tension was recorded. The probe was cleaned after each measurement by washing with copious amounts of distilled water and placed on a drop of distilled water again to ensure that the probe was not contaminated. If the surface tension of the distilled water did not read 72.8 ± 0.5 dyn/cm, the probe was cleaned by placing it over a Fisher burner.

Results and Discussion

Esterification of PVOH in Ionic Liquids. The modification of poly(vinyl alcohol) was carried out with the acid chlorides

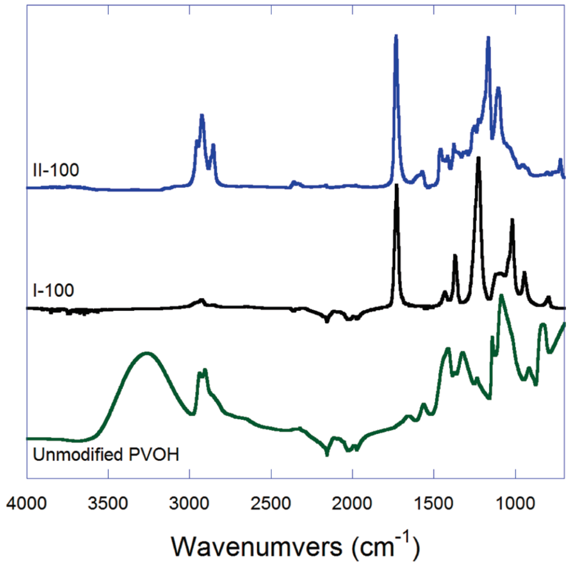

Figure 2. ATR-IR spectra of aliphatic acid chloride-modified poly(vinyl alcohol).

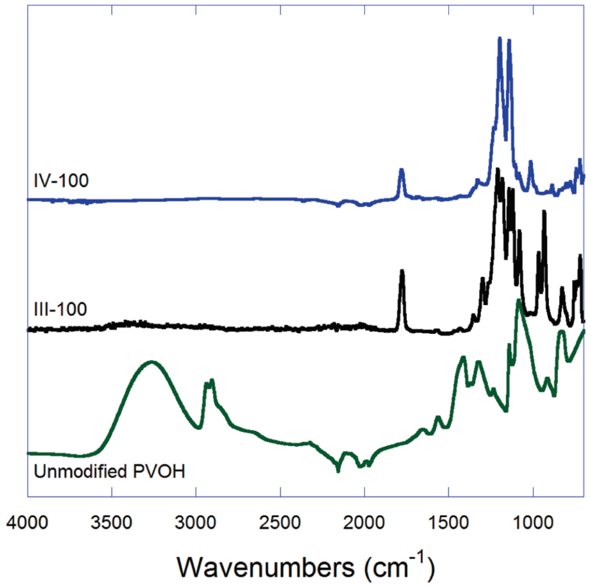

Figure 3. ATR-IR spectra of perfluorinated acid chloride-modified poly(vinyl alcohol).

shown in Figure 1, and we refer to the resulting polyesters by their associated roman numeral and corresponding extent of modification (for example, I-100 refers to 100% theoretical conversion, acetyl chloride-modified PVOH) . Esterifications carried out in BMIM-Cl were run both with and without pyridine catalysis to determine if there was any apparent difference in the reaction kinetics. All modification reactions were completed in less than 15 min regardless of catalyst loading; thus, BMIM-Cl is assumed to act as a catalyzing solvent for this reaction. IR analysis of the resulting polyesters suggests the complete conversion of the hydroxyl groups of PVOH to ester groups within 15 min at 90 °C without pyridine catalyst. In Figures 2 and 3 it is apparent that the −OH stretching vibration at 3200 cm^{-1} in the unmodified PVOH has completely disappeared, and prominent carbonyl stretching is observed at 1730 cm^{-1}. PVOH samples that were modified with perfluorinated acid chlorides also show C−F stretching at 1200 and 1150 cm^{-1}, characteristic of trifluoromethyl and difluoromethylene groups, respectively (Figure 3).

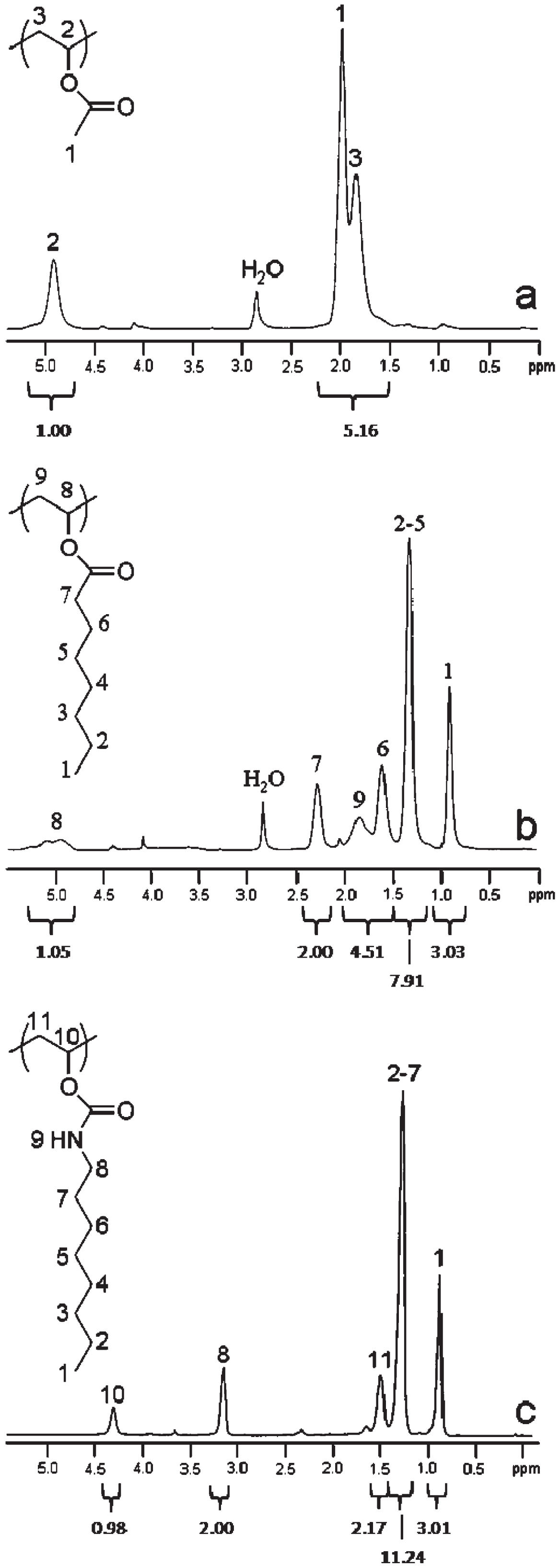

Figure 4. ^{1}H NMR spectrum of (a) acetyl chloride-modified PVOH (I-100, 100% conversion), (b) octanoyl chloride-modified PVOH (II-100, 95% conversion), and (c) octyl isocyanate-modified PVOH (V-100, 100% conversion).

The 100% modification of PVOH with acetyl chloride was further confirmed by NMR, whereas the modification of octanoyl chloride reached a conversion of 95% as calculated by the integration from Figure 4. Integration of the peaks near 5.0 ppm for each resulting polyester were compared with the peaks between 1.5 and 2.2 ppm and the peak at 2.3 ppm for I-100 and II-100, respectively, to determine percent conversion. While esterifications of PVOH with acid chlorides have been reported on, it is extremely difficult to obtain reaction yields of PVOH higher than 95%, and lengthy reaction times are necessary to reach these conversions.[26] The simple reaction conditions established for the esterification of PVOH in BMIM-Cl result in conversions ≥95% within 10−15 min. In addition, Figure 5 illustrates that the desired extent of modification can be easily controlled by simply adding the appropriate molar ratio of acid chloride to alcohol.

The esterification of PVOH in TBEP-DEP was also carried out and easily controlled, reaching similar conversions as demonstrated in BMIM-Cl. The reaction kinetics are only slightly slower than in BMIM-Cl as complete conversion of PVOH to the desired polyester can be obtained without pyridine catalysis in about 1 h at 90 °C. There are two advantages in using TBEP-DEP over BMIM-Cl. First, BMIM-Cl has a melting point around 70 °C, requiring elevated temperatures to dissolve PVOH and carry out these reactions, whereas TBEP-DEP is a liquid at room temperature and is therefore able to dissolve PVOH at room temperature, albeit very slowly. Second, complete conversion of PVOH to the desired polyester can be obtained at room temperature within 18 h. This allows for an added level of controllability when chemically modifying PVOH as the reaction kinetics can be tuned by adjusting the temperature of the reaction from room temperature to 90 °C and above.

Urethanation of PVOH in Ionic Liquids. Urethanation of PVOH carried out in TBEP-DEP resulted in quantitative, controllable conversion to the resulting polyurethane. The reaction kinetics are significantly slower (48 h at 90 °C) than the previously discussed esterification reactions, however, and the addition of dibutyltin dilaurate catalyst is required. IR spectroscopy suggests the quantitative and controllable conversion of PVOH to the resulting polyurethanes (Figure 6). The broad −OH band at 3200 cm^{-1} decreases in intensity as the narrower N−H peak at 3325 cm^{-1} increases in intensity with an increased extent of modification. As more urethane linkages are formed, the appearance of the other carbamate IR characteristics at 1578, 1612, and 1690 cm^{-1} are also apparent. The first two representative carbamate peaks are associated with the carbamate C−N and C−O, respectively, and the third peak is associated with the C=O stretch.

The NMR spectrum of the resulting octyl isocyanate polyurethane shown in Figure 4c confirms the 100% modification conversion from PVOH; however, one discrepancy in the spectrum is the absence of the peak for the N−H proton, which should appear typically between 5 and 6 ppm. The absence of this peak may be due to the rapid proton association/dissociation rate typical of this acidic carbamate proton. Integration of the peak near 4.3 ppm was compared with the peak at 3.2 ppm to determine percent conversion.

Urethanation of PVOH with octyl isocyanate was also attempted in BMIM-Cl; however, this solvent proved to be a poor reaction medium for urethanations as little to no reaction occurred.

Surface Analysis of Ionic Liquid and Polymer/Ionic Liquid Solution Surfaces. The surface activity of partially modified PVOH was studied by measuring changes in surface tension and chemical composition of ionic liquid/polymer solutions at various extents of modification. Table 1 summarizes the surface tension and chemical composition of the pure ionic liquid and the ionic liquid/polymer solutions before and after modification of PVOH. The naming scheme is the same as the previous modifications. The roman numeral indicates the modifying reagent, and the number indicates estimated polymer conversion based on the stoichiometric amount of reagent added to the solution. The denotation, "sol", indicates that the modified polymers were not isolated from the ionic liquid and left in solution for surface tension

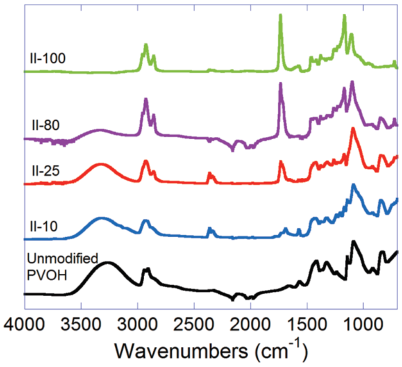

Figure 5. ATR-IR spectra of PVOH modified to varying extents with octanoyl chloride.

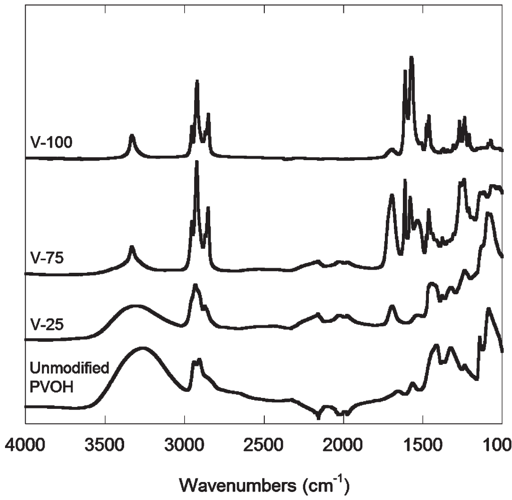

Figure 6. ATR-IR spectra of PVOH modified to various extents with octyl isocyanate.

Table 1. Surface Tension and XPS Atomic Composition Data for Ionic Liquid/Polymer Solutions

sample	surface tension (dyn/cm)	C (%)	F (%)	O (%)	N (%)	Cl (%)
pure BMIM-Cl	44.5	75.0	< 0.1	< 0.1	17.0	8.0
1% PVA in BMIM-Cl	45.0	74.9	< 0.1	1.5	16.9	6.7
II-5-sol	32.9	74.6	< 0.1	5.5	13.3	6.6
II-10-sol	30.3	74.4	< 0.1	6.3	12.8	6.3
IV-4-sol	24.5	56.6	19.2	4.7	11.8	5.7
IV-7-sol	20.3	57.2	23.9	4.1	10.1	4.7
IV-15-sol	18.8	54.5	27.5	4.5	9.7	3.9

measurements. The incorporation of 1 wt % PVOH in BMIM-Cl does not appreciably change the surface tension of pure BMIM-Cl; however, minimal esterification with either octanoyl chloride or perfluorooctanoyl chloride drastically reduces the surface tension of the ionic liquid. Perfluorooctanoyl substituents, having the lower surface energy, decreases the surface tension to a greater extent than the octanoyl moiety. In addition, increasing the extent of modification also decreases the surface tension further and increases the fluorine content at the ionic liquid/air interface for perfluorinated octanoyl chloride-modified PVOH (Table 1).

The observed trends for surface tension and chemical composition are expected of low surface energy moieties that are adsorbed to the liquid/air interface; however, there are two possible scenarios that could explain these same observations. One scenario is that the partially modified PVOH is adsorbed to the interface as intended. An alternative possibility is that the adsorbed material is a miniscule fraction of impurity or unreacted reagent that is present in the sample, leading to the same expected observations. While it may be possible that the reduction in surface tension is due to an impurity, we believe that it is, in fact, the partially modified polymer that is contributing to the observed surface characteristics for two reasons. First, we have shown that for the isolated, modified polymers all esterifications of PVOH are quantitative and complete within 15 min, suggesting minimal side reactions, and that unreacted reagent should not be present. Second, XPS is a high-vacuum technique typically limited to the analysis of solid samples. Typically liquids, organic small molecules, and moieties with an appreciable vapor pressure would be removed at the working pressures within the XPS instrument ($10^{-6}-10^{-8}$ Torr). This suggests that a small molecule impurity is not likely. Ionic liquids, on the other hand, have a negligible vapor pressure thus can be analyzed under high-vacuum techniques.

Conclusions

1-Butyl-3-methylimidazolium chloride and tri-*n*-butylethylphosphonium diethylphosphate have been found to be viable solvents and inert reaction media for the modification of poly(vinyl alcohol) under simple reaction conditions. The solubility of PVOH in TBEP-DEP is confirmed by dynamic light scattering. Although the dynamic light scattering results for 1% PVOH/BMIM-Cl are inconclusive, we are certain that PVOH is also soluble in BMIM-Cl. Both BMIM-Cl and TBEP-DEP were demonstrated to facilitate the quantitative esterification of PVOH without the aid of additional catalyst. The reaction kinetics of the esterification reactions presented here are significantly faster than previously reported in the literature, as complete conversion can be achieved in under 15 min in BMIM-Cl. While esterifications are slightly slower in TBEP-DEP (1 h), more controllability over the esterification reaction can be achieved as this solvent has a lower melting point than BMIM-Cl and can accommodate lower reaction temperatures and thus slower reaction rates.

Quantitative urethanation of PVOH has also been achieved in TBEP-DEP with reaction times comparable to current literature. BMIM-Cl did not, however, accommodate urethanation of PVOH under the specified reaction conditions.

The broader purpose of partially modifying PVOH with low surface energy substituents was to assess the surface activity of the resulting modified polymers in solution. Initial results indicate that we have systematically lowered the surface tension and manipulated the surface chemical composition of the modified polymer/ionic liquid solution by varying the chemical composition and the extent of modification of the partially modified PVOH.

Acknowledgment. We thank the NSF-sponsored Materials Research Science and Engineering Center at the University of Massachusetts for support.

Supporting Information Available: A method used to analyze PVOH solutions via dynamic light scattering in water and in TBEP-DEP indicates that the PVOH is soluble in each solvent at a 1 wt % concentration; a hydrodynamic radius of PVOH was determined for each solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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