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Influence of casting solvent on phenyl ordering at the surface of spin cast polymer thin films

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ABSTRACT

Controlling the surface molecular structure of spin cast polymer films is important for the rational design of surface properties. However, the relationship between spin casting parameters and film surface molecular structure is poorly understood. We report that the surface molecular structure of spin cast homopolymers which contain phenyl groups is influenced by the solvent aromaticity, investigated by a nonlinear optical spectroscopy, sum frequency generation (SFG) vibrational spectroscopy. When phenyl groups were located in a linear polymer backbone, spin casting with aromatic solvents enhanced the phenyl SFG signal relative to when a non-aromatic solvent was used which suggests that the aromatic solvent induced the surface phenyl groups to be more ordered and/or to lie more perpendicular to the film surface. In addition, when alkyl structures were believed to be present at the solvent/air interface, alkyl structures were observed at the film/air interface which suggests that molecular structure at the solvent/air interface was carried to the film surface. The effects of solvent aromaticity on phenyl ordering at spin cast film surfaces can be explained by different molecular structures of polymer chains at solvent/air interfaces, preferential solvation of functional groups during evaporation, and re-orientation of bulky side groups at the polymer film/air interface.

1. Introduction

The molecular surface structure of thin polymer films influences many important surface properties such as wettability, adhesive strength, lubricity, and biocompatibility [1]. Fabricating polymer surfaces with defined surface properties thus require an understanding of how thin film fabrication methods and post-fabrication processing affect polymer surface structure at the molecular level. Although recent reviews have highlighted advances in the fabrication of micropatterned and nano-patterned polymeric surfaces [2], polymer surface modification with plasma treatment methods [3], and the solvent effect on the surface segregation in copolymer and polymer blend films [4], the detailed relationship between polymer thin film deposition methods and the resulting surface molecular structure remains poorly understood.

One of the most simple, established and reproducible methods of depositing thin, uniform polymer films is spin coating polymer solutions onto flat substrates. Spin speed, solvent selection, polymer concentration, and spin coating under a solvent-saturated atmosphere have been shown to influence film properties such as thickness, surface roughness, and bulk molecular order [5]. Rapid solvent evaporation during spin coating can trap non-equilibrium polymer chain conformations within cast films [6,7] , resulting in residual stress [8] and a smaller degree of entanglement than at equilibrium [9]. The trapped polymer chain conformations have been shown to resemble their solution conformation [10,11] which is dependent on the solvent quality [12].

The role of solvent used for spin casting organic conjugated polymers has been extensively studied due to the relationship between a bulk conjugated polymer's morphology and its optical and electronic properties [13–15]. Shi et al. reported a correlation between the aggregation state of poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene (MEH-PPV) in solution and the quantum efficiency of the spin cast polymer film [16]. Aromatic solvents were hypothesized to preferentially solvate the aromatic backbone which led to aggregation of the alkyl side chains in the solution while non-aromatic solvents were hypothesized to expose the alkyl side chains to the solvent. Spin casting with non-aromatic solvents resulted in more polar polymer film surfaces than when aromatic solvents were used. The decrease in surface polarity when an aromatic spin casting solvents was used was likely due to the benzene ring lying perpendicular to the surface which

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decreased the surface concentration of polar methoxy groups [16]. However, there was no direct molecular level experimental evidence to confirm the conclusion.

The objective of this work was to investigate whether there is a correlation between the molecular surface structure of phenyl functional groups on spin cast polymer surfaces and the aromaticity of the solvent used for spin casting. In order to investigate the surface molecular structure of the films, the surface sensitive nonlinear optical laser technique sum frequency generation (SFG) vibrational spectroscopy was used in the study. SFG vibrational spectroscopy is a second order nonlinear optical technique that can selectively measure the vibrational spectrum of surfaces and buried interfaces [17–28]. Molecular functional groups at interfaces can be selectively identified because the SFG signal is enhanced when the frequency of the input IR beam and a SFG active vibrational mode are in resonance. In addition to detecting specific interfacial functional groups, SFG vibrational spectra provide information about interfacial molecular functional group orientation, orientation distribution, hydrogen bonding, and diffusion [29].

In this study, SFG spectra were collected from the surfaces of poly (phenyl methacrylate) (PPM), poly(benzyl methacrylate) (PBM), poly(methylphenylsiloxane) (PMPS) polysulfone (PSF), and poly(bisphenol A carbonate) (PBAC) films spin cast from aromatic and non-aromatic solvents. These polymers contain both aromatic and aliphatic functionalities with aromatic groups either in the side chains or in backbones. Chlorobenzene and chloroform, both of which dissolve many polymers used in organic solar cells and microelectronic packaging, were selected to compare a completely aromatic solvent to a non-aromatic solvent. Surface molecular structures were then correlated with different molecular structures of polymer chains at the solvent/air interface, preferential solvation of functional groups during evaporation, and migration of bulky side groups to the polymer film/air interface.

2. Materials and methods

2.1. Materials

Poly(phenyl methacrylate) (PPM) (M_w 100,000) was obtained from Scientific Polymer Products, Inc. poly(benzyl methacrylate) (PBM) (M_w 70,000), polysulfone (PSF) (M_w 35,000), and poly(bisphenol A carbonate) (PBAC) (M_w 64,000) were obtained from Sigma Aldrich, Inc. Poly(methylphenylsiloxane) (PMPS) (M_w 6000) was obtained from Gelest, Inc. To ensure that no spectral confusion could occur from the solvent, deuterated solvents were used in this study. Chloroform-d ($CDCl_3$) and chlorobenzene-d_5 (clb-d_5) were obtained from Sigma Aldrich, Inc. The molecular structures of the polymers and the solvents used in the research are plotted in Fig. 1 and the glass transition temperatures of the polymers are listed in Table 1.

2.2. Preparation of polymer thin films

Polymer samples were dissolved in solvents to form 2.0 wt% solutions. Calcium fluoride windows (ESCO Products, Inc.) were used for all SFG measurements and were cleaned in an oxygen plasma (PE-50, Plasma Etch) prior to sample preparation. A Speedline Technologies P-6000 spin coater was used to spin cast polymer solutions for 30 s onto the substrates. All films were held under vacuum overnight prior to measurements to remove any residual solvent.

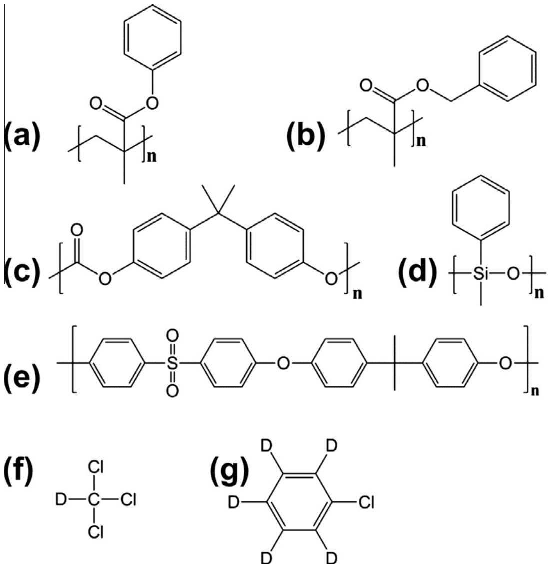

Fig. 1. Molecular structures of: (a) poly(phenyl methacrylate) (PPM), (b) poly(benzyl methacrylate) (PBM), (c) poly(bisphenol A carbonate) (PBAC), (d) poly(methylphenylsiloxane) (PMPS), (e) polysulfone (PSF), (f) chloroform-d ($CDCl_3$), and (g) chlorobenzene-d_5 (clb-d_5).

Table 1
Glass transition temperatures of the polymers used in this study.

Polymer	Glass transition temperature (°C)
Poly(methylphenylsiloxane)	−50
Poly(benzyl methacrylate)	54
Poly(phenyl methacrylate)	110
Poly(bisphenol A carbonate)	147
Polysulfone	185

2.3. Sum frequency generation vibrational spectroscopy measurements

The details of SFG theory and our SFG setup have been reported in previous publications [30–32]. The visible and IR beams passed through the back side of the window substrate and through the polymer film in a "face down" window geometry. The incident angles of the visible and IR input beams were 60° and 55° with respect to the substrate surface normal, respectively. The diameters of both input beams at the surface were approximately 500 μm. The pulse energies of the visible and IR beams at the sample stage were approximately 150 and 100 μJ, respectively. The reflected SFG signal from the surface was collected by a monochromator along with a photomultiplier and processed with a gated integrator. SFG spectra were collected using the ssp (s-polarized sum frequency output, s-polarized visible input, and p-polarized IR input) and ppp polarization combinations in the frequency range between 2700 and 3200 cm^{-1}.

2.4. SFG spectral fitting

The SFG signal intensity can be expressed by Eq. (1), where $\chi^{(2)}_{\mathrm{eff}}$ is the effective second order nonlinear optical susceptibility tensor of the surface and I_{IR} and I_{vis} are the intensities of the IR and visible input beams, respectively.

$$I_{\mathrm{SFG}} \propto |\chi^{(2)}_{\mathrm{eff}}|^2 I_{\mathrm{IR}} I_{\mathrm{vis}} \quad (1)$$

$\chi^{(2)}_{\mathrm{eff}}$ can be decomposed into the sum of a nonresonant (NR) term and a resonant (R) term described by Eq. (2). The resonant term can be modeled as the sum of Lorentzians when the input IR frequency is near a vibrational resonance where A_q, ω_q, and Γ_q are