



# Surface composition control via chain end segregation in polyethersulfone solution cast films



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## ARTICLE INFO

### Article history:

Received 1 September 2014

Received in revised form

8 December 2014

Accepted 13 December 2014

Available online 23 December 2014

### Keywords:

Polyethersulfone

Chain end segregation

Surface properties

## ABSTRACT

Surfaces and interfaces of polyethersulfone (PESU) materials play a crucial role in the overall performance of the polymer in applications such as filtration membranes, medical devices, and protective coatings. This work investigates the chain end localization to the polymer-air interface of solution cast films of semi-rigid rod PESU polymers end-capped with phenol (OH) and fluorescein isothiocyanate (FITC) groups. PESU solutions of varying molecular weight and low distribution were characterized via gel permeation chromatography (GPC) as well as static and dynamic light scattering. X-ray photoelectron spectroscopy (XPS) and confocal laser microscopy revealed a preferential localization of both –OH and –FITC chain ends to the PESU-air interface. Scaling of the chain end concentration as a function of polymer dimensions was determined to differ from that of flexible chain polymers. Surface analysis demonstrated that chain end chemistry could be used to tailor the nano- and macro-scale properties of the resulting PESU surface.

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## 1. Introduction

Polyethersulfone (PESU) is an engineering thermoplastic that is characterized by good optical properties, high thermal and chemical stability, mechanical strength, resistance to extreme pH values, and low creep [1]. PESU is an amorphous polymer with chain rigidity derived from the relatively inflexible phenyl and SO<sub>2</sub> groups and toughness generated by the connecting ether oxygen (Fig. 1) [2]. Major applications include filtration membranes, medical devices, and high performance coatings. For such applications, the properties desired at the polymer surface, such as adhesion, wettability, gas impermeability, low coefficient of friction, or biocompatibility, are often distinct from the bulk properties of the material. Typically, control of PESU surface properties for commercial applications is achieved by surface modification through various chemical or physical processes, such as plasma, chemical reaction, surface grafting, or metal coating [3–9]. These kinetically governed reaction mechanisms generally allow relatively little control over the equilibrium surface composition and structure. Additionally, such processes may be expensive and difficult to

model. It is also important that surface modification processes do not result in degradation of the bulk properties of the polymer.

One potential method to modify and control polymer surface properties is through the preferential segregation of functionalized chain-ends. Chain end segregation is driven by the balance between the free energy gain associated with the surface tension reduction and the free energy cost of demixing from the bulk, as governed by the classical Gibbs adsorption isotherm [10]. That is, it is energetically preferred for the lower surface energy component to be in contact with the zero surface energy medium such as air or vacuum [11]. In the case of an amorphous polymer, the random coil conformation is perturbed in the vicinity of a surface or non-interacting interface. To minimize the loss in conformational entropy, polymer chains ends may localize to the surface and thereby avoid the required “reflection” at the material boundary [12]. de Gennes has argued that the extent of chain end-segregation to a surface ( $\delta$ ) is controlled by the difference between the surface tension of an infinite polymer chain and that of the end-groups ( $\delta = \gamma_{\infty} - \gamma_{ce}$ ) [12,13]. When the ratio of  $\delta a^2$  ( $a$  representing the statistical segment length of the polymer) and the thermal energy ( $kT$ ) is on the order of unity, all chain ends within a distance of  $2R_g$  (coil diameter) from the surface will be localized to the surface. For this case, the volume fraction of chain ends in a near surface layer of thickness  $d$  is: [12,13]

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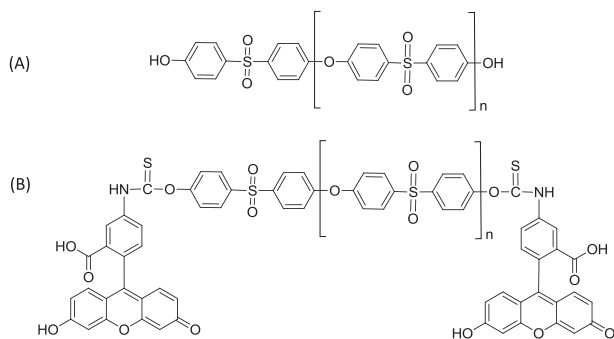


Fig. 1. A) -OH end-capped PESU and B) -FITC end-capped PESU.

$$\phi_{\text{surface}} = \phi_{\text{bulk}} \left( \frac{2R_g}{d} \right) = 2N^{-0.5} \left( \frac{a}{d} \right) \quad (1)$$

where  $N$  is the degree of polymerization. Therefore, as the distance from the surface ( $d$ ) approaches the coil diameter ( $2R_g$ ) the volume fraction of chain ends will reach the bulk value. This has been supported by several theoretical approaches, including mean-field calculations, self-consistent mean-field calculations, and molecular dynamics (MD) and Monte Carlo simulations, which predict chain end segregation [14,11,15–18].

Several studies have provided experimental proof of the surface segregation of polymer chain ends as well as the length scale of the concentration gradient that arises as a result of the segregation. Fluorocarbon-terminated polystyrene (PS-F) is the most widely studied model system, as the fluorinated chain ends offer strong contrast with the polymer backbone and can drastically alter surface properties. Combinations of neutron reflectivity (NR), X-ray photoelectron spectroscopy (XPS), static secondary ion mass spectroscopy (SSIMS), and contact angle analysis have shown that chain ends in PS-F systems adsorbed preferentially at the surface [19–24]. Elman et al. observed surface enrichment of fluorinated end groups with damped, oscillatory concentration profiles providing best fits to NR data [21]. The periodicity of the oscillations was on the order of the unperturbed polymer chain dimensions for polymers with fluoroalkyl end groups, while fluorosilane-terminated polymer showed larger periodicity, indicating that the polymer backbone was extended near the air-polymer interface. Schaub et al. demonstrated that the surface coverage of fluorocarbon chain ends was greater than 20% in thin film blends of PS and PS-F [20]. Tanaka et al. reported the surface segregation of chain ends to the polymer-air interface in  $\alpha$ - $\omega$ -fluoroalkyl-terminated polystyrenes with various molecular weights using NR and XPS [23]. Model analysis of angular-dependent XPS (ADXPS) results revealed that the surface chain end concentration ([CE]) was higher than the corresponding bulk value with lower molecular weight systems showing the highest [CE]. Depth profiles showed a surface segregation layer of the chain end groups followed by a depletion layer beneath it. Beyond the depletion layer, the bulk [CE] was recovered ( $\sim 2R_g$  from the surface). Wong et al. studied the surface reorganization of polystyrenes terminated with fluorsilane and carboxylic acid end groups using ADXPS [25]. They reported a preferential segregation of chain ends to the polymer air interface, and suggested that the length scale for segregation was dependent on molecular weight and scaled roughly with the  $R_g$ . Studies of poly(dimethylsiloxane) and perfluoropolyether modified systems showed similar chain end surface segregation.

The majority of the reported experimental and theoretical studies have focused on the behavior of flexible, idealized chains that adopt random coil conformations. It has not been established if structural constraints of a semi-rigid/rigid rod polymer backbone,

like that of PESU, will allow conformational rearrangements similar to those of flexible chains and follow established models for flexible polymer chain-end segregation. The length scale of the concentration gradient that arises as a result of chain end segregation is also a matter of debate, and it is expected that chain rigidity will play a role in its determination. Previous studies have demonstrated effects of chain end chemistry on the macro-scale surface properties such as wettability and surface energy, while relatively little is known about the effects of chain end segregation on nano-scale surface properties of amorphous polymer surfaces. Although PESU displays high chain rigidity, long PESU chains form amorphous rather than crystalline films, and thus the polymer is predicted to exhibit deviations from bulk segmental density distribution near the surface due to the localization of chain ends to the polymer-air interface. In this paper, we report the extent of chain end segregation to the PESU-air interface in films cast from solutions of polymers with narrow molecular weight distributions prepared by fractional precipitation. Two different chain-ends of varying size and properties were investigated: small, hydrophilic phenol (OH) end-groups and bulky, hydrophobic fluorescein isothiocyanate (FITC end-groups) (Fig. 1). Polymers were characterized by gel permeation chromatography, static and dynamic light scattering, and UV-Vis spectroscopy. Films were analyzed by XPS, atomic force microscopy, contact angle goniometry, and confocal laser microscopy. The [CE] depth profile was determined and the length scale of segregation was estimated and compared with that predicted by flexible-chain models. Experimental results were correlated with MD to explore predictability of chain end segregation as a function of end group structure in PESU films. The effects of the chain end composition and molecular weight on nano- and macro-scale surface properties are also reported. Significant differences in surface roughness, modulus, coefficient of friction, wettability, and surface energy were observed, indicating the potential utility of chain end segregation as a means of controlling surface properties of PESU films.

## 2. Experimental

### 2.1. Materials

PESU was supplied by Solvay Specialty Polymers USA, L.L.C. in a white powder form. The PESU chains were end-capped with functional phenol (OH) groups ranging from 50 to 200 micro-equivalents/g according to titration. This polymer is commercially available under the trade name Virantage®PESU (Fig. 1). The reported tensile modulus for PESU is 2.7 GPa [26]. Fluorescein isothiocyanate (FITC) fluorescent probes were obtained from Sigma-Aldrich in a sealed container and stored in a refrigerator in order to prevent photo-bleaching and moisture exposure. Deuterated  $N$ - $N$ -dimethylformamide (d-DMF) was supplied by Sigma-Aldrich and stored in a desiccation chamber until use. Anhydrous DMF, anhydrous toluene, and anhydrous methanol (MeOH) were obtained from Sigma-Aldrich. Anhydrous solvents were supplied in sealed bottles and were removed through a syringe to avoid laboratory exposure. In each case that a polymer solution was filtered, a Whatman polytetrafluoroethylene (PTFE) membrane filter (0.25  $\mu\text{m}$  pore size) was used.

### 2.2. Sample preparation

#### 2.2.1. Fractionation

Polymer solutions of 5 wt% PESU in DMF were prepared for fractionation. PESU powder was dried in a vacuum oven at 120  $^{\circ}\text{C}$  for 1 h prior to dissolution. PESU/DMF solutions were kept in an oil bath set to 25  $^{\circ}\text{C}$  in order to maintain the temperature during

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