Polymer 132 (2017) 198–205

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Synthesis and dynamic de-wetting properties of poly(arylene ether sulfone)-*graft*-poly(dimethyl siloxane)

Kunzhi Shen, Heng Hu, Jiandong Wang, Guojun Liu*

Department of Chemistry, Queen's University, 90 Bader Lane, Kingston, Ontario K7L 3N6, Canada

ARTICLE INFO

Article history:
Received 16 August 2017
Received in revised form
1 November 2017
Accepted 3 November 2017
Available online 6 November 2017

Keywords:
Coatings
Anti-smudge
Polymer grafting
Click chemistry

ABSTRACT

Many test liquids cleanly glide down crosslinked coatings bearing nanopools of a grafted liquid ingredient for dewetting enablement (NP-GLIDE coatings) at low substrate tilt angles. It was unclear if an engineering plastic with a high glass transition temperature Tg could replace a crosslinked coating matrix to support an NP-GLIDE coating. This paper reports the uniform grafting via click chemistry of liquid poly(dimethyl siloxane) (PDMS) onto poly(arylene ether sulfone) (PAES, $T_g = 185$ °C) to yield graft copolymers PAES-*g*-PDMS with low polydispersity indices. Hexadecane droplets (5 μL) cleanly glided down at sliding angles (SAs) of less than 3 ± 1° on all of the coatings prepared from PAES-*g*-PDMS with PDMS weight fractions of 3.4%, 19%, 30%, and 40%, respectively. Further, an oil-based ink readily contracted on them. The sliding angle of 15 μL droplets decreased from 47 ± 2° to 13 ± 1° as the PDMS weight fraction increased from 3.4% to 30%.

1. Introduction

Grafting a low-surface-tension liquid polymer such as poly(dimethyl siloxane) (PDMS) [1–4] or a perfluorinated polyether (PFPE) [5] onto one component of a polyurethane (PU) or an epoxy formulation and curing the resultant compound with the other components of a PU or an epoxy formulation yields an NP-GLIDE PU or epoxy coating. Here the term NP-GLIDE derives from the observation that many test liquids had no problem to glide down such a coating at substrate tilt angles of less than 5° and that the coating contains nanopools of a grafted liquid ingredient for dewetting enablement. Further, these coatings are anti-smudge because marker inks and paints readily contract on them and the contracted ink patches are easily removed. Additionally, the coatings are transparent because the nanopools of the anti-smudge agent on the surfaces and within the matrices of the coatings are much smaller than the wavelengths of light and do not readily scatter light. The coatings have the further advantage of being wear tolerant because the uniform removal of the surface layer from the coating ruptures the nanopools in the coating matrix and replenishes the newly exposed surface with fresh anti-smudge chains. These advantageous features of the NP-GLIDE coatings provide them with excellent potential for numerous applications such as on windows of skyscrapers or windshields of automobiles.

Our NP-DLIDE coatings were inspired by prior reports of grafted liquid-like monolayers [6–9] and of slippery liquid-infused porous surfaces (SLIPS) [10–17]. On a SLIPS [10–17], a test liquid that is incompatible with the pore-filling liquid readily slides because the frictional or pinning force exerted by the latter on the former is very weak. The pinning force rendered by a grafted liquid-like PDMS or PFPE monolayer on a test liquid is also weak, thus endowing these coatings with excellent liquid sliding performance as well. An NP-GLIDE coating has similar liquid-sliding properties as a grafted liquid-like monolayer because it also features on its surface a grafted liquid-like layer. However, it is much thicker than a monolayer with thickness reaching tens of micrometers just like that for a SLIPS. NP-GLDE differs from a SLIPS in that the infusing liquid polymer is covalently attached to the coating matrix.

Previously, the PU and epoxy coating matrices that were used to host the nanopools of anti-smudge agents were crosslinked. Engineering plastics such as poly(arylene ether sulfone) (PAES), possessing excellent chemical resistance, mechanical properties, and high glass transition temperatures (T_g) are widely used in industry and by consumers. We wondered about the possibility of rendering anti-smudge properties to engineering plastics and producing NP-GLIDE engineering plastics. To investigate this possibility, we grafted PDMS onto PAES, an engineering plastic with a T_g of 185 °C, to yield PAES-*g*-PDMS, where *g* denotes *graft* [18]. PAES was

---

* Corresponding author.
E-mail address: gliu@chem.queensu.ca (G. Liu).

https://doi.org/10.1016/j.polymer.2017.11.008

selected because of our prior experience in preparing and using PAES graft copolymers for membrane applications [19–21]. The prepared PAES-*g*-PDMS samples with PDMS weight fractions of 3.4%, 19%, 30%, and 40% were then dissolved in a solvent and cast onto glass plates to yield the coatings. Reported here is our preparation of well-defined PAES-*g*-PDMS via click chemistry and the de-wetting properties of the resultant coatings.

We note that there have been many reports on the modification of PAES to improve its processability [22], solubility [23], hydrophilicity [24], hydrophobicity [25], biocompatibility [26] and other properties. For example, electrophilic sulfonation has been performed on the PAES backbone to introduce hydrophilic groups for the production of proton exchange membranes for fuel cell applications [27] and water treatment [28]. The quaternization of tertiary amines via chloromethyl groups on PAES yielded graft copolymers suitable for preparing anion exchange membranes [29]. Aside from modifying pre-made PAES, functionality has also been introduced via functional monomers that could be polymerized via condensation with bisphenol A and bis(4-chlorophenyl) sulfone, for example, to yield PAES containing functional groups in the backbone [30]. The condensation strategy is especially useful if one wishes to produce block copolymers. For example, telechelic poly(ethylene oxide) has been condensed with telechelic PAES oligomers to yield multiblock copolymers of the two homopolymers [31]. Telechelic PDMS has also been co-condensed with telechelic PAES to yield multiblock copolymers of PAES and PDMS [32–36]. Due to the poor compatibility between non-polar PDMS and the relatively polar PAES, it has been difficult to use high-molecular-weight macromers for these reactions and to obtain samples of low polydispersity. A third approach to modify PAES is to graft another polymer unto a PAES backbone to yield graft copolymers [19–21,26,37–41]. For example, PAES-*g*-PDMS has been synthesized for gas separation and was achieved via the hydrosilylation of vinylsilylated PAES with hydrosilyi-terminated PDMS [37]. We note that the polydispersity of the reported PAES-*g*-PDMS copolymers ranged between 4.0 and 6.2 and their surface properties were not reported.

We prepared PAES-*g*-PDMS using the reactions depicted in Scheme 1. Some 10% of the repeat units of a commercial PAES sample were first chloromethylated. The introduced chloride groups were then replaced by azide moieties using sodium azide as the nucleophile. Meanwhile, a commercial PDMS-OH sample, with PDMS bearing one terminal hydroxyl group, was reacted with 4-oxo-4-(prop-2-yn-1-yloxy)butanoic acid to introduce a terminal alkyne group, yielding PDMS-≡. A varying amount of PDMS-≡ was subsequently reacted with the azide-bearing PAES to produce the targeted graft copolymer PAES-*g*-PDMS$_{x\%}$ with $x\%$ denoting the weight fraction of PDMS in the final polymer and taking values of 3.4%, 19%, 30%, and 40%, respectively.

2. Results and discussion

2.1. Precursor polymer synthesis and characterization

Despite the availability of alternative literature methods for grafting polymers onto PAES [20,26,31,37–41], we used click chemistry as depicted in Scheme 1 to graft PDMS onto PAES because of its relatively mild reaction conditions and high efficiency. To partially chloromethylate the AES units, paraformaldehyde was reacted with PAES in the presence of $SnCl_4$ and $(CH_3)_3SiCl$ following a literature method [29]. The benzyl chloride groups were then converted to benzyl azide groups via nucleophilic substitution with azide [42]. Fig. S1 shows a ^{1}H NMR spectrum and signal assignments for a partially chloromethylated PAES sample. By comparing the integration intensities of the chloromethyl signal at 4.53 ppm with that of the four *ortho* proton signals near 7.85 ppm corresponding to the phenyl rings sandwiching the sulfonyl group, we determined that the polymer exhibited a chloromethylation degree of 10%.

The chloromethylated PAES was then treated with sodium azide. After this reaction, the methylene signal in the bottom spectrum in Fig. S1 shifted from 4.53 to 4.26 ppm and this shift indicated that the chloride had been replaced by the azide group.

Fig. S2 compares the SEC traces of PAES, chloromethylated PAES, and azidated PAES. The three peaks were similar in shape. However, the second and third samples shifted somewhat to the higher molecular side. Our quantitative analysis yielded the PS-equivalent molecular weights listed in Table 1. The data were consistent with the anticipated products at each reaction step.

PDMS-≡ was synthesized via the esterification of PDMS-OH with 4-oxo-4-(prop-2-yn-1-yloxy)butanoic acid [43]. NMR evidence for the successful synthesis of PDMS-≡ is shown in Fig. S3, where ^{1}H NMR spectra in the region of interest for PDMS-OH and PDMS-≡ are compared. The disappearance of the “a” signal corresponding to PDMS-OH and our other quantitative analyses indicated that the conversion was quantitative.

2.2. PAES-g-PDMS synthesis and characterization

PDMS was grafted onto PAES via a click reaction between PDMS-≡ and azidated PAES. We note that this click reaction has been used to graft other polymers onto PAES [19,44–46]. In previous cases, DMF was always used as the solvent because it is a good solvent for both azidated PAES and CuBr. However, PDMS-≡ is insoluble in DMF. Since azidated PAES has been reported to be soluble in THF [47] and THF is also a good solvent for PDMS, we started by performing the click reaction in THF.

Fig. 1 shows a SEC trace of a PAES-*g*-PDMS$_{x\%}$ sample prepared in THF with a targeted x% value of 25% that was recorded before the reaction mixture was extracted with hexanes to remove unreacted PDMS-≡. Using the number-average molecular weight of 5.1×10^4 Da for azidated PAES and 5.0×10^3 Da for PDMS-≡, our calculations suggested that an average of 3.4 PDMS side-chains should be attached onto each PAES backbone if the click reaction was quantitative. Comparing this SEC trace with that of the azidated PAES precursor, which is also shown in Fig. 1, revealed that the peak maximum of the former did not move much relative to that of the latter, though the former bore a broad shoulder on the higher molecular weight side. This result suggested that PDMS was not uniformly grafted onto PAES and the reacted mixture consisted of unreacted azidated PAES and PAES-*g*-PDMS. We further note that a residual negative peak characteristic of unreacted PDMS-≡ was observed, suggesting that the reaction was incomplete. We have attempted to improve the situation in vain by increasing the reaction time from overnight to 48 h. We also tried to replace PMDETA with 2,2′-bipyridine as the ligand or reduced the CuBr and PMDETA concentration by half.

We note that high polydispersity values reaching 6.0 have also been reported by Nagase et al. [36] for their prepared PAES-*g*-PDMS samples. Their samples were also prepared in THF but via the hydrosilylation of vinylsilylated PAES with hydrosilyl-terminated PDMS.

We suspected that the strange SEC traces for the crude PAES-*g*-PDMS samples prepared in THF were due to the nonuniform grafting of PDMS onto PAES and the latter situation arose because of the insufficient solvation of the azidated PAES chains in THF. Because they were marginally soluble and incompatible with PDMS, the azidated PAES chains could segregate from PDMS-≡ to form submicron domains that were rich in each of the two components. This phenomenon has been well established for other