

Preparation of End Grafted Polyacrylonitrile Brushes through Surface Confined Radical Chain Transfer Reaction

Feng ZHOU, Shu Juan LIU, Bo WANG, Ting Mei WANG, Miao CHEN*, Wei Min LIU

Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000

Abstract: End grafted polyacrylonitrile (PAN) brush was prepared through surface initiated polymerization *via* the chain transfer process. The thiol-terminated monolayer and PAN brushes were characterized by FTIR, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), ellipsometry and contact angle measurements *etc.* It is demonstrated that radical chain transfer reaction and surface initiated precipitate polymerization can be used to prepare end-grafted polymer brushes.

Keywords: Surface initiated polymerization, chain transfer, polymer brush, acrylonitrile.

Surface Initiated Polymerization (SIP)^{1,2,3} is an attractive method for the modification of substrate surface aiming to gain a control of the interface properties such as biocompatibility, wettability, lubrication *etc.* The key step is to introduce initiating points on substrate surfaces, which can be carried out through the assembly of self-assembly-initiators or *in-situ* modification of end group functionalized surfaces by using self-assembling techniques⁴. In this article we will demonstrate for the first time that polyacrylonitrile brush can be grafted from substrate surface by using surface initiated precipitate polymerization *via* the chain transfer process.

Mercaptopropyltrimethoxysilane (MPS) is used to prepare thiol terminated silicon wafer (denoted as HS-silicon) according to the silane assembly chemistry^{4,5}. The transfer of thiol hydrogen to the propagating radical chains in bulk solution followed by reinitiated polymerization, whereby a thiol radical adds to a monomeric double bond, would result in end-grafted polymer brushes. HS-silicon has the water contact angle of 70°, indicating a complete coverage of thiol-terminated monolayer. Polymerization was carried out in a 20 mL mixture of acrylonitrile (AN), azo-diisobutylnitrile (AIBN, initiator) and THF at 60°C for a certain time in the presence of HS-silicon. The molar ratio of AN: AIBN (100:1) and the volume ratio of AN: THF (1:2) were kept constant. Precipitate was found after polymerization occurred because of not so good solubility of PAN in THF. The polyacrylonitrile-modified substrate (denoted as PAN-silicon) was rinsed ultrasonically with a large amount of THF to remove the unbounded species.

The FTIR of thiol terminated SAM, thus-prepared PAN brush and also the spin cast

*E-mail: miaochen@isl.ac.cn

PAN film as a control for the selected region between 3200 and 1500 cm^{-1} are illustrated in **Figure 1**. HS-silicon shows the stretching vibration of C-H at 2825 and 2927 cm^{-1} , proved successful assembly of MPS. After polymerization, the absorbance bands that characteristic of PAN ($\nu_{\text{C}\equiv\text{N}}$: 2242 cm^{-1} ; $\nu_{\text{C-H}}$: 2870 cm^{-1} , 2930 cm^{-1} , 2948 cm^{-1}) appeared and greatly consisted with the spin cast PAN film, indicating that AN was grafted onto silicon wafer.

Figure 1 Transmittance FTIR spectra of (a) self-assembled monolayer of MPS; (b) end grafted PAN brushes and (c) the spin-cast PAN film

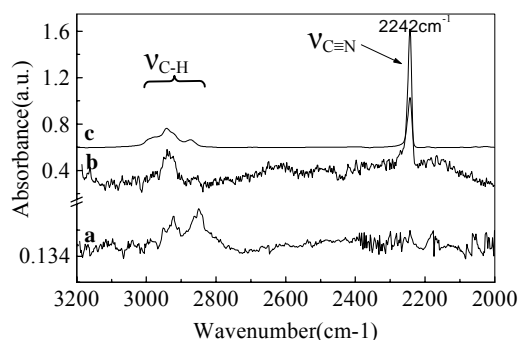
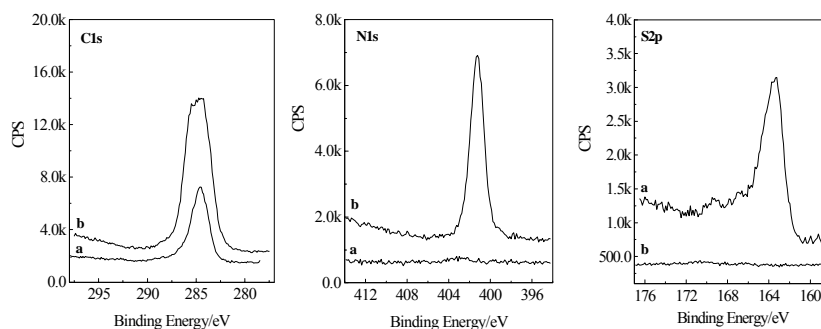


Figure 2 XPS spectra of C_{1s} , N_{1s} and S_{2p} of HS-silicon (a) and PAN-silicon (b)



The reaction strategy is also verified by XPS (**Figure 2**). Grafting polymerization of AN onto HS-silicon is confirmed with the broadening and blue shift of C_{1s} peak at 284.6 eV to 285.3 eV and also the appearance of N_{1s} at 401.1 eV. S_{2p} at 163.3 eV that was obvious for HS-silicon could not be detected after grafting polymerization for 24 h. This indicated that the substrate was completely covered by a polymer layer of at least 5 nm (In fact, the brush thickness was about 135.6 nm).

The variation of brush thickness with the polymerization time is shown in **Figure 3**. Grafting polymerization is found to nearly complete within the first four hours. More than 135 nm thick PAN brush is obtained with 24 h of polymerization time. The water contact angle decreased from 70° to about 42° that is characteristic of PAN brush. The

contact mode AFM topography of a 135 nm thick PAN brush revealed a homogeneous and relatively smooth polymer brush with an RMS roughness of 1.584 nm (**Figure 4**).

Figure 3 Variation of contact angle (Δ) and thickness (\square) with polymerization time

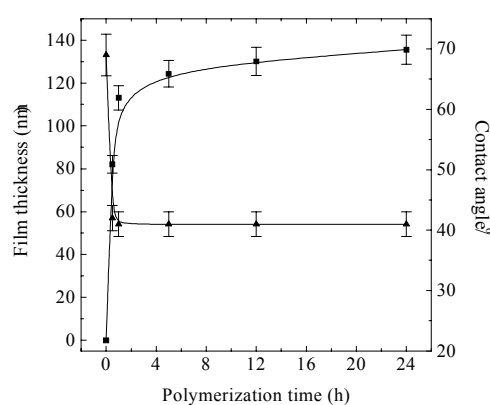
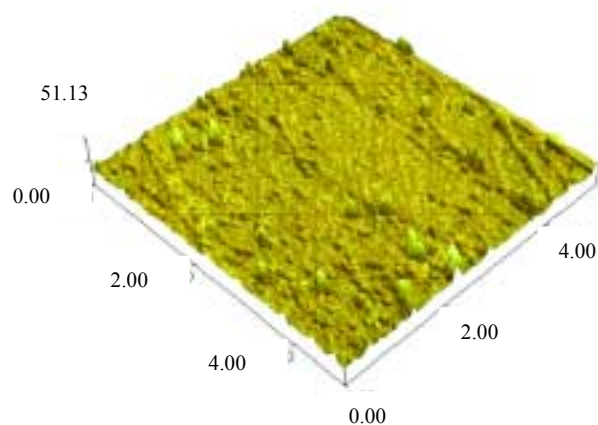


Figure 4 AFM topography of the 135.6 nm thick PAN brush



In conclusion, we have demonstrated PAN brush can be prepared by surface initiated precipitate polymerization *via* the radical chain transfer process. The method is a new addition to surface initiated polymerization and is different from the ever reported methods by combining SIP and precipitate polymerization. It can be applied to the surface modification of materials for micro/nano-electromechanical systems (MEMS/NEMS).

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