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Surface initiated supplemental activator and reducing agent atom transfer radical polymerization (SI-SARA-ATRP) of 4-vinylpyridine on poly(ethylene terephthalate)

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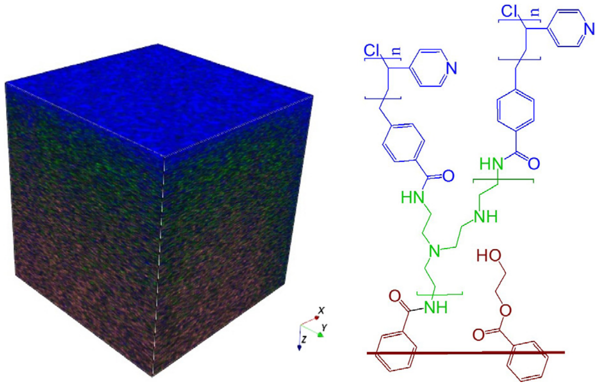
GRAPHICAL ABSTRACT



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ABSTRACT

Poly(ethylene terephthalate) (PET) substrates were modified by means of surface-initiated supplemental activator and reducing agent atom transfer radical polymerization (SI-SARA-ATRP) of 4-vinylpyridine (4VP). Substrates were pretreated in order to graft chloromethylbenzene (CMB) units capable of initiating the radical polymerization reaction of 4VP units. Surface characterization techniques, including Water Contact Angle (WCA), Attenuated Total Reflection (ATR), X-ray photoelectron spectroscopy (XPS), Atomic Force Microscopy (AFM) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) showed a successful grafting of a stable, smooth and homogenous layer of p4VP. This process offers the advantages of a rapid, simplified and low cost strategy to chemically modify polymer substrates with covalently bonded layer of the pH responsive p4VP for different applications. Moreover, by using TOF-SIMS profiling, we were able to track a density gradient along the z-axis generated by the interpenetrating phases of the different layers of the final modified surface. Fact that we correlated to the various positions of initiation sites within the polyethylenimine (PEI) used for PET aminolysis prior to CMB grafting. Our strategy will be used in future work to graft other polymers for different applications where industrial scale viable options are needed.

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1. Introduction

Several application fields are pushing the limits of high-quality functionalized surfaces, especially in biosensing, heterogeneous catalysis, etc. Pyridine based polymers gained much interest due to various applications such as water soluble polymers and coordination reagents for transition metals [1]. Polymerization of 4VP by atom transfer radical polymerization (ATRP) is quite challenging because 4VP is a coordinating monomer that can compete for the binding of the metal catalysts. To avoid this problem, a much stronger ligand like tris(2-pyridylmethyl)amine (TPMA) should be used in the polymerization system. Surface initiated ATRP (SI-ATRP) of 4VP was reported on polysulfone surface [2], and Cu^0 mediated polymerization of 4VP was reported on silicon wafer using a copper plate in DMSO [3]. In the present work, we used surface initiated SARA ATRP to build p4VP from PET surface. This work takes advantage of the abundant and recyclable PET as substrate and largely simplify the modification procedure so as to offer a very cheap and viable option for large scale production of high-quality specialized materials.

Poly(ethylene terephthalate) (PET) is a well-known polyester. With a yearly world production exceeding 50 Mtons, it is one of the most used polymeric materials, especially in the textile and packaging industries, due to its good mechanical strength, toughness and fatigue resistance at elevated temperatures. PET was produced by transesterification of dimethylterephthalate and ethylene glycol, with methanol being the byproduct. The direct esterification of terephthalic acid and ethylene glycol then took over due to a higher reaction rate, no need for a transesterification catalyst, lower cost, higher molecular weight obtained and water being a byproduct instead of methanol [4]. The constant improvement in PET recycling mainly through hydrolysis [5] made PET one of the most recycled and reused polymers. The ester moiety in PET is subject to different chemical reactions, including transesterification, aminolysis, hydrolysis and many others [6]. Reusability, good mechanical properties, and the reactivity of PET, makes it a preferred material in different forms (films, fibers, fabrics…) for applications where tailored functional surfaces are needed without scarifying good bulk properties [7–13]. In this work, PET is modified through consecutive aminolysis, initiator grafting then surface initiated living radical polymerization of 4VP.

It is acknowledged now that reversible-deactivation radical polymerization (RDRP) had taken polymer chemistry into a new level [14] where polymer architecture can be controlled like in traditional ionic polymerization [15,16] while taking advantage of the tolerance and functionalities of radical polymerization. Three types of RDRP have gained momentum, nitroxide-mediated polymerization (NMP) [17], reversible addition–fragmentation chain transfer polymerization (RAFT) [18] and atom transfer radical polymerization (ATRP) [19,20], the latter being the most studied and versatile, where reaction control is maintained through an equilibrium between two oxidation states of a metal-ligand complex, most often Cu^I-L/Cu^{II}-L. Nevertheless, ATRP suffered from few drawbacks that limit its versatility, especially with its oxygen sensitivity that lead to the unavoidable buildup of the higher oxidation state Cu^{II} and therefore hard degassing techniques like freeze-pumpthaw cycles are used, the non-stable Cu^I has to be purified before each reaction and relatively high load of catalyst has to be used in order to compensate for the lost copper species throughout the reaction, increasing the cost of posttreatment to remove excess catalyst. These drawbacks stand especially in the way of scaling up the reaction to industrial levels. Several strategies were proposed to minimize copper loading [20], where dissolved oxygen is removed from the system and accumulated Cu^{II} is reduced back to Cu^I using electric potential, photoreduction, or chemical reductant like conventional initiators, Sn^{II} species, ascorbic acid, hydrazine and zerovalent metals [21–29]. The process of continuously reducing the Cu^{II} is labeled under activator regenerated by electron transfer (ARGET)-ATRP [25]. When considering the industrial viability of these different reducing agents, the metallic copper is most interesting due to its low cost, compatibility with different polymerization systems, and its simple removal especially when used in a heterogeneous form (wire, tube…), facilitating industrial scale implementation. Metallic copper mediated RDRP was investigated and two different reaction mechanisms were suggested. One proposed mechanism, supplemental activator and reducing agent atom transfer radical polymerization (SARA ATRP), has Cu^I as the major activator of alkyl halides, Cu^0 acting as a supplemental activator, and both by inner-sphere electron transfer (ISET). Another proposed mechanism called single electron transfer living radical polymerization (SET-LRP) assumes that the Cu^I species do not activate alkyl halides, but undergo instantaneous disproportionation, and that the relatively rapid polymerization is due to a fast reaction between alkyl halides and Cu^0 through an outer-sphere electron transfer (OSET). Researchers have debated about the mechanism of copper-mediated RDRP in the presence of Cu^0 [30–32]. A detailed study of the two mechanisms was conducted by the Matyjaszewski group [33,36] where the kinetic experiments agreed more with SARA ATRP (Fig. 1) rather than SET-LRP.

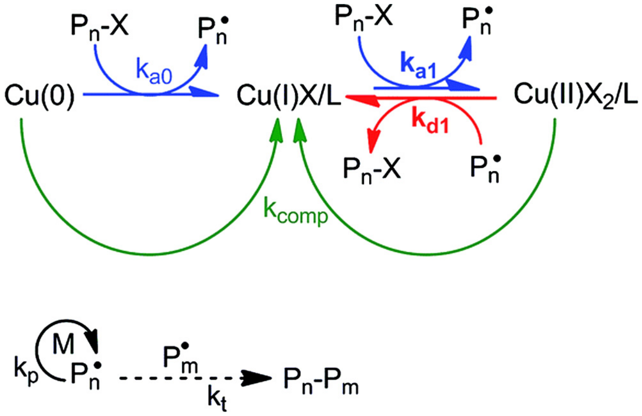

Fig. 1. General mechanism of SARA ATRP (Ref. [37]).

In this paper, surface initiated SARA-ATRP was used to grow p4VP chains on PET surface simply and efficiently according to the easy low-cost strategy previously described. Characterization techniques such as WCA, XPS, AFM, SEM and ToF- SIMS, were used to explore the physical, chemical, dimensional, and morphological properties of modified surfaces after each step. Homogenous, smooth and reproducible p4VP layer was shown to be covalently grafted onto the substrate.

2. Experimental section

2.1. Materials

PET films (Melinex 0D - 125 μm) were obtained from DuPont Teijin films. Branched polyethylenimine PEI (average Mw ~25,000), triethylamine (Et_3N, >99.5%), copper (II) chloride (Cu_2Cl, 98%), 4-vinylpyridine (4VP) were obtained from Aldrich. Et_3N was distilled from KOH and 4VP was passed through basic alumina to remove the inhibitor. Orange II (Orange 7 acid), 4-(chloromethyl) benzoyl chloride (>98%), Tris(2-pyridylmethyl)amine (TPMA, >98%) were obtained from TCI Chemicals and used without further purification. Copper (0) wire (d = 1.0 mm, annealed, 99.9%) was