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Surface-initiated reversible addition–fragmentation chain transfer polymerization from "clickable" polypropylene surface modified by iodine plasma activation

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ABSTRACT

An iodine modified polypropylene surface was synthesized by iodine plasma activation. The obtained polypropylene surface was found to be a useful platform for secondary reactions. For instance, an azide-functionalized PP was prepared by nucleophilic exchange reaction. The surface was proven to be reactive toward R group of an alkyne modified RAFT agent via the copper-catalyzed azide–alkyne cycloaddition. RAFT mediated graft polymerization of methacrylic acid was carried out and lead to a controlled polymerization from the surface. Characterizations of the modified surface and the grafted polymers were performed through FTIR-GATR, XPS, AFM and colorimetric assays.

1. Introduction

Surface modification of polymers with brushes is nowadays widely investigated to tailor surface properties [1,2]. Polymer brushes can be prepared following two main strategies: the "*grafting to*" and the "*grafting from*" strategies. The "*grafting to*" strategy involves the attachment of pre-synthesized polymers via a reactive end group to a functionalized surface. This experimentally straightforward method involves low grafting densities due to steric hindrance of reactive surface sites by already graft polymers.

The "*grafting from*" strategy (also called "surface-initiated polymerization") involves the attachment of an initiator or an agent onto the surface and the polymerization of a monomer from this modified surface. The polymer chains synthesized from the surface lead to the formation of dense polymer brushes.

The initiator attachment can be challenging when the surface exhibit high inertness such as polypropylene (PP). Plasma treatment offers an attractive and highly versatile tool for preparing functional polymers. Furthermore, halogen compounds are widely used as leaving groups for nucleophilic substitution in organic chemistry and efficiency of bromine or brominated derivative plasma treatment [3,4] onto polymer surfaces has been proven. However, brominated compounds are also known for their very high toxicity and their use should be therefore limited whereas the use of iodine could be an alternative [5]. Due to the higher polarizable bond, subsequent nucleophilic substitution reaction is faster with C—I than for C—Br bond. To the best of our knowledge, iodine plasma treatment on polymer surface has not been extensively studied [6].

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Then, the nucleophilic exchange of halogen by azides groups allows the use of cycloaddition reaction proposed by Sharpless [7]. This cycloaddition was widely used for the grafting of RAFT agents onto silica particles through a chemical way [8]. It could be applied for the grafting of RAFT agents onto polymer surfaces through a plasma activation. Grafting RAFT agents onto a surface gives the opportunity to polymerize a wide range of monomers when choosing the adapted transfer agent, giving finally brushes at the surface [9]. In the case of RAFT polymerization, the choice of the RAFT agent for a given monomer is of peculiar importance for the success of the controlled radical polymerization. The efficiency of RAFT agents is determined by the nature of the R and Z [10] substituents and their choice is critical for a surface polymerization approach. The RAFT agent must contain a reactive moiety in order to be grafted onto the surface [10]. Then, the RAFT agent can be grafted on the surface either by the Z or the R group.

In case of polymerization with a RAFT agent grafted by the Z group, no propagation occurs from the surface. This method is often assimilated to a "*grafting to*" method since the propagation step occurs only in solution. The main drawback results in the fact that the growing chain must diffuse through the polymer layer to react with the RAFT agent grafted on the surface. During the polymer brush growth, the accessibility of the RAFT agent is limited and a high brush density cannot be obtained. On the contrary, grafting by the R group leads to greater brush density onto the modified surface [11]. Finally, experimental conditions during polymerization (nature of the solvent, temperature, stirring) should not degrade the surface.

Size exclusion chromatography is the main technique used to highlight the control of the polymerization performed in solution but it cannot be applied to polymerizations performed from surfaces. The control of the polymerization onto a surface is relatively tricky when the modified surface is a polymer surface compared to perfectly flat surface such as silicon wafer. This control from polymer surfaces has been proven by indirect characterization techniques such as gravimetry [12], X-ray photoelectron spectroscopy [13], ellipsometry [14].

In this article, we describe an original and versatile modification of an inert polymer though an iodine plasma treatment to produce reactive polypropylene surfaces. These last were used for further RAFT polymerization in order to prepare polymer brushes. According to this strategy, the surface was first activated by iodine plasma and the resulting iodine groups from the surface were converted into azide ones by nucleophilic substitution. RAFT agent was then grafted using the well-known azide–alkyne cycloaddition (Fig. 1). Finally, poly(methacrylic acid) brushes were then obtained via surface initiated RAFT polymerization.

2. Experimental section

2.1. Materials

Polypropylene (PP) was supplied by Greiner Bio-one for the microplates (96 Well, F-bottom, Chimney Well), by Goodfellow, UK for PP sheets (1.5 ∗ 300 ∗ 300 mm), by SICAM geotextiles, France for PP nonwoven fibers (8.4 mg, 0.7 mm diameter, fiber diameter 25 μm). 4-cyano-4-thiothiopropylsulfanylpentanoic acid (CTPPA) was synthesized as described in the literature [15]. All others reagents, were purchased from Sigma–Aldrich.

2.2. Plasma treatment

The plasma reactor consisted of two cylindrical parallel aluminum electrodes (diameter: 13 cm, distance between electrodes: 6 cm) placed in cylindrical vessel coupled with a RF-generator (13.56 MHz) and equipped with an efficient vacuum pump (18 m^3/h flow rate, initial pressure inside the device was 4 Pa). Prior to plasma treatment, all polypropylene samples were washed in an ultrasonic bath successively with acetone and ethanol during 90 s and finally dried in an oven at 60 °C. Then the PP samples were set between the electrodes of the reactor. The pressure of the reactor was adjusted to 4 Pa. Polypropylene surface was first treated by argon plasma (10 W, 90 s, 40 Pa). The plasma reactor was equipped with a vial containing solid iodine and separated from the reactor by a screw valve. The valve was slowly opened after argon pretreatment. Iodine was sublimated and then introduced into the plasma reactor. Treatment with iodine plasma was performed by varying the plasma reaction time at a power of 100 W. After iodine plasma exposure, samples were then exposed to a sweeping stream of iodine for a time equal to the exposure time. After surface treatment, the vacuum pump was stopped and argon

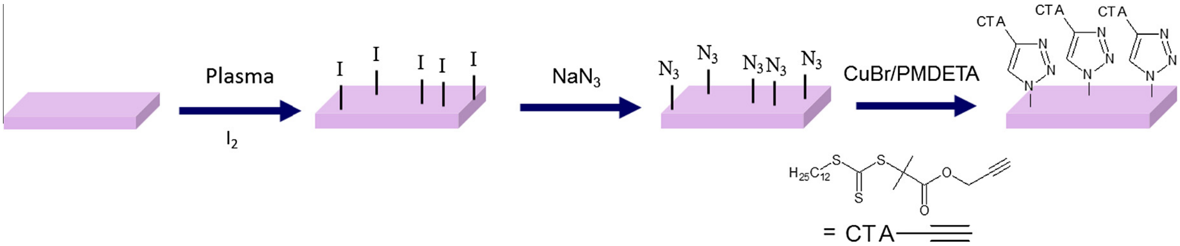

Fig. 1. Modification by "Click chemistry" of iodine plasma activated PP surface.