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Full paper

Molecular structure engineering of dielectric fluorinated polymers for enhanced performances of triboelectric nanogenerators

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ABSTRACT

Fluorinated polymers have been widely used in triboelectric sensors, displays, and energy harvesting devices because of their superior electron affinity, which leads to the negative triboelectric materials. While previous reports have shown that the control of dielectric constants of fluorinated polymers can increase the triboelectric output performance, the exact relationship between the molecular structures of fluorinated polymers and the resulting triboelectric properties is still elusive. In this study, we demonstrate that the molecular chain structures of the fluorinated polymers depending on the number of fluorine units, the molecular weight (M_w), and conditions such as spin rate and annealing temperature directly affect the relative dielectric constants of dielectric layers and the triboelectric polarity, which are closely related to the triboelectric output performance. We observe that the polymer chain packing structures result in the increase of the relative dielectric constants, thus leading to the improvement of triboelectric output currents. Among the fluorinated polymers used in this study, a poly (2,2,2-trifluoroethyl methacrylate) polymer with three fluorine units and M_w of ~ 20 kg/mol shows the best triboelectric output performance. Our molecular engineering strategy to control the dielectric constants of fluorinated polymers can be a robust platform for the fundamental studies of triboelectric materials and their applications in diverse energy harvesting and sensing devices.

1. Introduction

Engineering the molecular structures of polymeric materials with fluorinated units provides unique characteristics including low surface energy, high thermal stability, and excellent electrical and optical properties [1], and enable a variety of applications from surface coatings [2] to optoelectronic device applications [1,3]. Recently, fluorinated derivatives have been widely used in triboelectric sensors [4,5] or displays [6,7] and in energy harvesting devices [8,9] because of their superior electron affinity, which leads to the negative triboelectric materials. Triboelectric devices operate on the basis of the effects of contact electrification and electrostatic induction [9,10]. When the fluorinated polymers are in contact with other positive triboelectric materials, opposite (negative and positive) charges are generated on each surface because of contact electrification. Subsequently, when the two surfaces are separated, the triboelectric surface charges induce the compensating charges on each electrode attached to the triboelectric materials via electrostatic induction, thus causing current to flow through the external circuit. The output performance of triboelectric nanogenerators strongly depends on various factors including the choice of materials with high polarity difference in the triboelectric series, as well as the contact area and the chemical structures.

For the choice of materials with high polarity difference in the triboelectric series, while nylon and metals (aluminum, gold) are frequently used as positive triboelectric materials, fluorinated polymers such as polyvinylidene fluoride (PVDF) or polytetrafluoroethylene (PTFE) derivatives are mainly used as negative triboelectric materials for triboelectric energy harvesting and sensing applications [11–14]. To enlarge the effective contact area between positive and negative tribosurfaces, various surface micro- and nanostructures have been investigated [9,15]. Furthermore, for the increase of surface charge density, the chemical modifications of triboelectric surfaces have been introduced by direct surface treatments such as atomic-level functionalization using halogen-containing silane units [6,16–18] or plasma/ion-injection treatment on the surface of PTFE or polyethylene terephthalate (PET) [19,20]. Engineering the dielectric properties of

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triboelectric materials is an another way to enhance the triboelectric output performance. Recently, several approaches have been reported to improve the triboelectric performance by tuning the internal structures of dielectric polymer materials based on polymer-nanoparticle composites [21] and porous structures in dielectric materials [22,23], and by the corona-discharging of multilayered dielectric films [24]. These approaches can tune the dielectric constants for the improvement of the triboelectric output performance. The dielectric constants of polymers can also be controlled by the grafting polymerization of fluorinated polymers [25,26]. Recently, fluorinated grafting polymers based on polyvinylidene difluoride–grafted poly(tert-butyl acrylate) copolymers (PVDF-*g*-PtBA) were reported to enhance the performances of triboelectric devices [27]. Although previous reports have shown that the control of dielectric constants can increase output performance, the exact relationship between the molecular structures of fluorinated polymers and the resulting triboelectric properties is still elusive. In particular, although the additional F atoms in fluorinated polymers are known to increase the charge density [28], the systematic study of their effects on the dielectric constant and the resulting triboelectric performances has not been reported.

In this study, we synthesize fluorinated polymers with a controlled fluorine unit and molecular weight (M_w) by reversible addition-fragmentation chain-transfer (RAFT) polymerization to systematically investigate the relationship between the molecular structures of fluorinated polymer films and the resulting triboelectric output performance together with the relative dielectric constants and triboelectric polarity. We investigate the molecular chain structures that depend on the number of fluorine units, the M_w, and process conditions such as spin rate and annealing temperature. We find that there is a critical number of fluorine units for the enhanced dielectric constant of fluorinated polymers and the resulting triboelectric performance. The relative dielectric constant of the fluorinated polymers increases with increasing fluorine units in the polymers (zero to three fluorine units for poly (ethyl methacrylate) (PEMA) to poly(2,2,2-trifluoroethyl methacrylate) (PTF)), and then slightly decreases when the number of fluorine unit is over three (poly (2,2,3,3,3-pentafluoropropyl methacrylate) (PPF) and poly (2,2,3,3,4,4,4-heptafluorobutyl methacrylate) (PHF)). This behavior of dielectric constant variation depending on the number of fluorine units matches the results of the triboelectric output currents. We also find that the molecular weight (M_w) and spin-coating rate of fluorinated polymers influence on the polymer chain packing structures and the resulting dielectric constant and triboelectric output performances. To our knowledge, this work is the first study to investigate the effects of fluorine units and the process conditions of dielectric polymers on dielectric constants and triboelectric output performance.

2. Results and discussion

Fig. 1a shows a triboelectric device using fluorinated-polymers and poly (L-lysine) (PLL) as negative and positive triboelectric materials, respectively. Fluorinated-polymers with different numbers of fluorine units and M_w were synthesized by RAFT polymerization as summarized in Table S1. For comparison, PEMA including the same chemical backbone of the fluorinated polymers without fluorine units was used

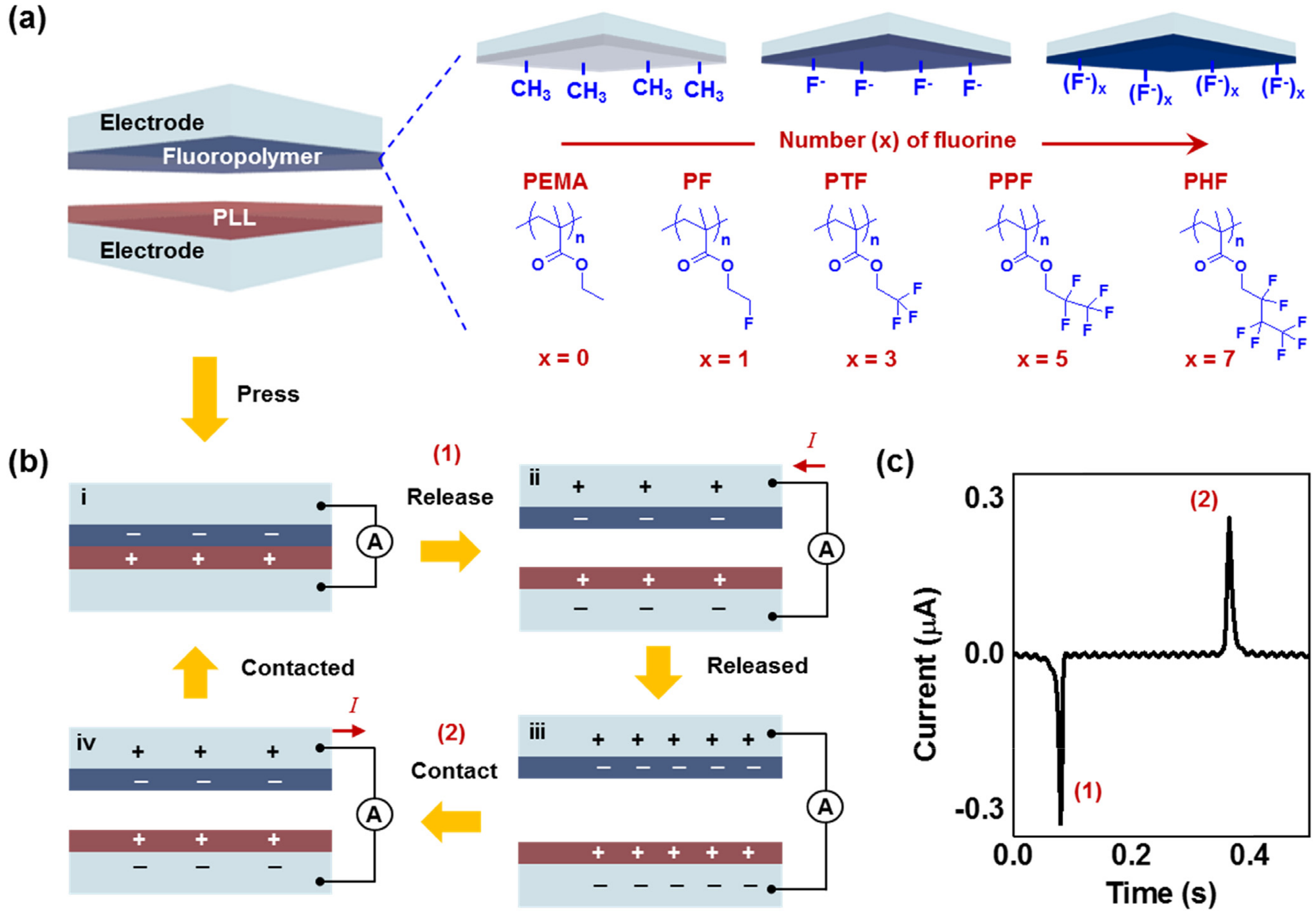

Fig. 1. (a) Schematic illustration of a triboelectric nanogenerator based on fluorinated polymers with different kinds of fluorine units, and (b) its working mechanism. The cyclic contact (iv and i) and separation (ii and iii) between the fluorinated and PLL-coated films induces charge separation and transfer, thus leading to current flow through the external circuit. (c) Representative triboelectric output current. Peaks (1) and (2) appear when both of the coated surfaces are contacted and separated, respectively.