Synthesis of hydrogen-bond-enriched, fluorescent and triboelectric hyperbranched polymers via Michael addition reaction

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Abstract. It is very meaningful to realize color recognition and mechanical-electrical energy conversion in one material simultaneously, which is very essential in improving the equipment of border guards. However, simultaneously endowing one material with color regonition and mechanical-electrical energy conversion presents challenges because they result from different mechanism. Herein, a series of hyperbranched polymers, HP9, HP10, and HP11, were synthesized via the Michael addition reaction to solve the dilemma. Extensive hydrogen bonding was embedded into these hyperbranched polymers, so that the polymers exhibit good triboelectrification ability. The voltage output is about 347 V, the current output is about 2.8 µA, and the charge quantity is about 150 nC, respectively. Moreover, the polymers display excellent fluorescence under 365 nm ultraviolet light based on the mechanism of aggregation-induced emission (AIE). Furthermore, the thermodynamic behavior and mechanical properties of the hyperbranched polymers can be regulated by adjusting the content of the hard segments. The Young's modulus and strength gradually increase with the increase of the hard segment unit. The Young's modulus, strength and toughness of HP10 are 3.72 MPa, 2.69 MPa and 19.55 MJ/m3, respectively. The combination of fluorescence and frictional electrification will have great application potential in the equipment of border guards.

Keywords: hyperbranched polymer, Michael addition reaction, aggregation-induced emission, triboelectric nanogengerator.

1. Introduction

It is a crucial problem for soldiers and mountaineers that suppling power and illumination at night, especially in extreme environments where temperatures are freezing[1-2]. The dilemma faced by these people has become an international issue since soldiers need more safety guarantees as well as mountaineers require more portable equipment. For illuminations and identifying coating in darkness, fluorescent materials are suitable choices since only UV lights are needed for the luminescence of such materials. Besides, electricity is essential for heating and communicating wirelessly. Thus, combining the needs for illumination and power, and integrating functions of fluorescence and electricity generating are two main challenges.[3]

Recently, fluorescent materials have been extensively studied and applied to a variety of fields like biosensing, cell imaging, and dyes[4-7]. They are also designed to have different properties suitable for different usage showing photoluminescence phenomena. According to the luminescent principle, fluorescent materials can be divided into two types: aggregation-induced emission (AIE) and aggregation-caused quenching (ACQ)[8]. The former restricts intramolecular rotation through the aggregation effect to achieve fluorescence emission,9 while the latter achieves fluorescence quenching due to aggregation destroying energy level jumps and the latter needs only to be distributed in a single molecule to show significant fluorescence characteristics10.

As a common AIE group, tertiary amine in solution systems has attracted extensive attention in recent years, and colorful displays can be obtained by adjusting its solution concentration[11-13]. However, the luminescent behavior of tertiary amino groups in bulk materials has been studied rarely.

Additionally, introducing a large number of primary and secondary amines into the material can also obtain a large number of hydrogen bond donors, which can form extensive hydrogen bonds with atoms of higher electronegativity such as oxygen atoms, and endow the materials with higher modulus

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and strength[14-15]. On the other hand, polar groups such as primary or secondary amines will enhance the electron-losing ability of the material, which makes polymer materials rich in primary and secondary amines often have excellent triboelectrification capabilities, such as nylon[16-17], which has been demonstrated the significant triboelectrification behavior with other various polymeric materials, namely the triboelectric nanogenerator (TENG)[18-21]. This inspired us to introduce primary amine, secondary amine, and tertiary amine atoms into one material at the same time, which will not only endow the material with excellent fluorescent light-emitting ability but also improve the triboelectric ability, resulting in integrating luminescence and electric energy collection and realize the energy supply for border guards and mountaineering enthusiasts.

In this paper, a new hyperbranched material that has a large number of hydrogen bonds and many tertiary amines is developed, which provides the material with features like aggregation-induced emission and applicability for triboelectric nanogenerators. It shows good mechanical performance with Young's modulus of 3.72 MPa and a strength of 2.69 MPa. Also, the hyperbranched polymer displays excellent AIE fluorescence at the wavelength of 400 nm and good voltage output when contact separation with polytetrafluoroethylene (PTFE). The voltage output is about 347 V, the current output is about $2.8 \ \mu$ A, and the charge quantity is about 150 nC, respectively. The excellent triboelectricity and fluorescent properties make this hyperbranched polymer have good application prospects in the field of equipment for border guards and mountaineering enthusiasts.

2. Experimental

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2.1 Materials

Methacrylamide, isophorone diisocyanate, bis(2-aminopropyl) polypropylene glycol and polytetrafluoroethylene (PTFE) were bought from Aladdin (Shanghai, China). Triethylamine and tetrahydrofuran were purchased from J&K scientific. All reagents were commercially available and used as supplied without further purification.

2.2 Synthesis

First, methacrylamide was dissolved in tetrahydrofuran solvent and then the isophorone diisocyanate was added dropwisely at the N2 atomosphere, the molar ratio of the two was set as 2:1. The mixture was stirred for 1 hour. After the solvent evaporated, a white powder was obtained, namely the hard segment.

Second, the obtained hard segment was dissolved in tetrahydrofuran and the bis(2-aminopropyl) polypropylene glycol was added dropwisely at the N2 atomosphere, the molar ratio of the two was set as 9:10, 10:10 and 11:10 respectively. The mixture was stirred for 24 hour. Finnally the mixture was dried at 60°C for 24 hours to gain the hyperbranched polymers. Thus the specimens are named as HP9, HP10 and HP11 depandant on the molar ratio of the two chemicals.

2.3 Characterization

The chemical structure were characterized by a FTIR (Nicolet 6700, Thermo Scientific), operating in transmission mode from sample films cast onto KBr disks. Thermogravimetric Analyzer (TGA) experiments were carried out with a TA instruments' TGA209F1 with a heating rate of 20 °C/min from 50 to 700 °C. Differential scanning calorimetry (DSC) was carried out with NETZSCH DSC214, a cyclic heating/cooling run programme was taken under the rate of 10 °C/min at the temperature of -100 to 160 °C. Mechanical properties conducted at room temperature by using an MTS (2 kN) tensile machine. Five specimens of each composition were tested, the data reported were the average values. The resistance change were collected by electrometer (Keithley 6514). The fluorescence emission spectrum tested by Fluorescence spectrometer (FL3-111, HORIBA).

3. Results and discussion

3.1 Molecular Design

The challenge of introducing the excellent triboelectricity and fluorescence into the polymeric material is to embed extensive hydrogen bonds and tertiary amines. Thus, a hyperbranched structure that confined the formation of intermolecular hydrogen bonds and branched points, namely the tertiary amines, need to be constructed in this work. Under this circumstance, the presence of tertiary amines will not hinder the formation of hydrogen bonds. Besides, due to the absence of crosslinked network structure in hyperbranched polymer, it should be thermplastic and can be re-precessed.



Figure 1. Synthesis route of hard segment.

Therefore, the methacrylamide and isophorone diisocyanate (IPDI) was selected to react first to synthesis the hard segment, which can be used to form strong intermolecular hydrogen-bond. The synthesis route of the hard segment can be found in Figure 1. This reaction will convert an isocyanate group into a urea group, which enabled the formation of intramolecular hydrogen bonds. Then, the hyperbranched polymer was synthesized by Micheal addition reaction between the synthesized hard segment and bis(2-aminopropyl) polypropylene glycol (BPPG). Figure 2 shows the mechanism of the Micheal addition reaction between amine and acrylamide. Furthermore, Figure 3 shows the target hyperbranched polymeric structure. Here, the nitrogen atoms form tertiary amine connecting three molecules. For comparison, more hyperbranched polymer are formed according to varied amounts of hard segments. Differing the proportion of hard segment, compared with fix amount of IPDI, products were named HP9, HP10, and HP 11. For HP9, the ratio between the hard segment and IPDI added was 9 to 10, and the other two products followed this rule of naming.



Figure 2. Mechanism of Michael addition reaction used in this work. H_{2N}





3.2 Structural Analysis

The molecular structure of the hard segment can be verified by the comparison of the FTIR of the IPDI and the hard segment (Figure 4). The disappearance of signal near 2250 cm-1 suggested the isocyanate group of the IPDI unit had reacted completely, while a new signal appeared at 3200-3350 cm-1 indicating the presence of secondary amine and tertiary amine. Furthermore, the signal that appeared at 1600-1750 cm-1 presented carbonyl groups, showing an absorption that inclines towards the lower wavenumber, meaning the presence of hydrogen bonds. The hydrogen bond interaction occurred both intermolecular and intramolecular, responsible for the strength and capability for applying for the triboelectric nanogenerator.



Figure 4. FTIR spectra of hard segment and IPDI, respectively.

In order to study the thermal stability of such hyperbranched polymer, the thermogravimetric analysis was carried out for HP9, HP10, and HP11 respectively, as shown in Figure 5. It revealed that the temperature of decomposition of HP9, 10, and 11 is around 337-345 °C, and the mass keep unchanged until 300 °C, suggesting such hyperbranched polymer are thermostable, and feasible for enduring relatively high temperatures. The thermodynamic performance of such hyperbranched polymers can be evaluated by the DSC, as shown in Figure 6. The results pointed out that the glass transition temperature (Tg) of HP0, HP10 and HP11 is about -30 °C, -5 °C and 10°C respectively. Obviously, in such hyperbranched polymers, the higher the hard segment, the more the hydrogen bond formed, thus the Tg is related with the movement of PPG segment, which will be constrained by the hydrogen bond.



Figure 5. The curves of mass versus temperature of the hyperbranched polymers.



Figure 6. DSC heating curves of the hyperbranched polymers.

3.3 Mechanical properties

In Figure 7, the graph shows the typical stress-strain curves of such hyperbranched polymers. Clearly, with the increase of hard segments in the hyperbranched polymer, it becomes stiff and robust. The Young's modulus increases from 3.15 MPa to 8.86 MPa as well as the strength increase from 1.36 MPa to 3.84 MPa for HP9 and HP11 respectively. The details of mechanical performance can be found in Table 1. Interestingly, with the PPG content increase, the elongation at break increasing gradually, which is 943%, 1175, and 1478% for HP11, HP10 and HP9, respectively. Although Young's modulus, strength and elongation at break change linearly with the PPG content, the toughness of HP10 and HP11 are similar, ~19.55 MJ/m3. Therefore, after comprehensive consideration of the glass transition temperature and the comparison of mechanical properties, HP10 is selected as the research object to further study its triboelectric behavior and fluorescence characteristics.



Figure 7. The stress-strain curves of the hyperbranched polymers.

Table 1. The mechanical performance of the hyperbranched polymers.

| Samples | Young's modulus (MPa) | Strength (MPa) | Elongation at break (%) | Toughness (MJ/m3) |
|---------|-----------------------------|-------------------|----------------------------|----------------------|
| HP9 | 3.15 | 1.36 | 1487 | 15.57 |
| HP10 | 3.72 | 2.69 | 1175 | 19.55 |
| HP11 | 8.86 | 3.84 | 943 | 19.91 |

3.4 AIE fluorescence and TENG

It has been known that the n- π^* interactions among electron-rich groups show a non-conventional emission, namely the AIE phenomenon.[22] Therefore, a large number of tertiary nitrogen atoms will produce significant fluorescence. In this work, the molecular branches of hyperbranched polymers contain a large number of tertiary nitrogen atoms, and these atoms will aggregate in large quantities due to the influence of intermolecular interaction (hydrogen bonds), thereby producing significant fluorescence. Figure 8 shows that the HP10 specimen has obvious blue luminescent characteristics under 365 nm ultraviolet light. The fluorescence spectrometer recorded the emission bands of HP9, HP10 and HP11, and the strongest light intensity was located at 400 nm, which is in line with the observed fluorescence color display, proving that the hyperbranched polymer had remarkable fluorescence emission ability.



Figure 8. The digital photo of the HP10 under 365 nm UV lamp (left) and Fluorescent spectra of the hyperbranched polymers (right).

Furthermore, when one polymer contains extensive hydrogen bond donors and it is in contact with the external interface, it will be positively charged because it is easy to lose electrons. For example, nylon and polyurea often have positive charges after friction with polytetrafluoroethylene, the greater the hydrogen bond density, the higher the amount of charge generated [23-24]. In this work, the hyperbranched polymer contains a large number of primary and secondary amine groups, and the hydrogen atoms connected to the nitrogen atoms have high activity. When in contact with other materials, they tend to be positively charged due to the loss of electrons. In order to verify the physical process, it was in contact with PTFE and used copper foil as an electrode. Copper was used for its good conductivity which enabled charge to flow and thus generate electricity[25]. The principle is shown in Figure 9: when HP10 and PTFE are in the initial separation state, there is no charge flow in the external circuit (Figure 9a), and when HP10 and PTFE are in contact, due to PTFE has a stronger electronegativity, HP10 is easy to lose electrons, result a negative charge in PTFE due to the electrostatic induction effect, while HP10 has a positive charge (Figure 9b); in the subsequent separation process, because both excellent PTFE and HP10 are insulators, so their surface charges cannot be conducted in time. Therefore, there will be electrostatic induction with the copper electrode again, so that the copper foils will be positively charged and negatively charged (Figure 9c). Meanwhile, since the two copper foils are directly connected to the external circuit, a potential difference and current will be generated in the external circuit. When the separation distance is the largest, the charges of copper foil, PTFE and HP10 are in a balanced state, so there is no charge flow in the external circuit, and the voltage and current return to 0 (Figure 9d); when PTFE and HP10 come closer and gradually contact the process, the opposite charge will be induced again in the copper foil, and then the external circuit will be prompted to generate the opposite current, thus ending a cycle (Figure 9e and 9b), and this cycle will generate infinite AC charge.

Here, we recorded the voltage, current and electricity generated in this process and the results are shown in Figure 10, respectively. The voltage output is about 347 V, the current output is about 2.8 μ A, and the charge quantity is about 150 nC, respectively.



Figure 9. Schematic illustration of the TENG working mechanism.



Figure 10. The output performance of the TENG. (a) The voltage; (b) the current; and (c) the charges.

4. Conclusions

In summary, a series of hyperbranched polymers were synthesized based on the Michael addition reaction. The thermal behavior and mechanical properties of the hyperbranched polymers were regulated by adjusting the content of the hard segments. The Young's modulus and strength gradually increase with the increase of the hard segment unit. Interestingly, although HP10 and HP11 exhibit different strength and elongation at break, their toughness is similar, ~19.55 MJ/m3. Since the interior of the hyperbranched polymer is rich in hydrogen bonds, the polymer exhibits good triboelectrification ability. The voltage output is about 347 V, the current output is about 2.8 μ A, and

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the charge quantity is about 150 nC, respectively. Furthermore, because the polymer contains tertiary nitrogen atoms, it has excellent fluorescence. Due to the fluorescence on clothing made from these materials can warn team members of their partners' locations and help navigate terrain changes, preventing potential injuries in extreme environments. Additionally, joints movements allow the upper and lower layers in the TENG equipment, producing charges during movement, and thus store electricity which can heat inside clothes in extreme environments. Thus, the excellent triboelectricity and fluorescent properties make this hyperbranched polymer have good application prospects in the field of equipment for border guards and mountaineering enthusiasts.

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