Novel Thermochromic Copolymers with Two Luminescent Colors

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A new kind of thermochromic polymers with high fluorescence based on copoly(styrene-maleic anhydride) (SMA) and amino-substituted 1,8-naphthalimide is prepared by the condensed route. Accompanied their thermochromic process, the fluorescence of the copolymers will also change irreversibly from blue to green light when heated.

Thermotropic dyes have been found applications in the technically important field of thermographical processes such as thermopainting, textile process, medical treatment, printing etc.[1] Many scientists have found thermochromic materials among metals, metal oxides, double salts, complexes of organic materials, liquid crystals. In particular, thermochromic materials can be used for laser marking of polymers with a NIR laser as a heat source.[2] Nevertheless, there is a growing industrial interest in laser-marking because laser marking technology eliminates costs and environmental complications associated with inks, masks and other printing or stamping expendables, which are used for printing on polymers.[3] Hence, much effort had been made towards new suitable materials for laser marking.[3–5] For example, K. Müllen et al in 2000 synthesized a new kind of thermochromic dyes based on amino-substituted perylenedicarboximides; however, they were not polymer and hardly form uniform film.[5] On the other hand, in contrast to the compounds synthesized by us in this work, most of other thermochromic materials only have color changes between one real color and black or white when they are heated.

On the basis of the concept of the thermochromism of thermally unstable (di-*tert*-butoxycarbonyl)amino group,[5,6] we here describe an approach to get thermochromic polymers with high fluorescence based on copoly(styrene-maleic anhydride) (SMA) and amino-substituted 1,8-naphthalimide. When heated, the polymer changes its color and its fluorescence both as shown in Figure 1, and this process is accompanied by a large bathochromic shift in the absorption and fluorescent spectra. The copolymer SMA is a kind of commercial polymeric material with low cost. So it is widely used in various areas such as automobile materials, electronic household applications etc.[7] 1,8-Naphthalimides are well-known chromophores and have been widely used as brilliant fluorescent dyes for synthetic fiber and as electroluminescent materials.[8–10] The color including emission peak of 1,8-naphthalimides can be tuned by substitution on the 4-position of the naphthalimide ring.[11,12] Our idea of designing the novel thermochromic and fluorescent polymer dyes stems from a striking bathochromic color change that occurs if an electron-donating group such as amino group in this paper is attached to a chromophore.[5,12] A masking group, di-*tert*-butoxycarbonyl in this work, may drastically diminish the ability of the electron-donating substitute, so that the electron-donating group changes into an electron-withdrawing group. Furthermore, if di-*tert*-butoxycarbonyl is thermally cracked, the thermochromic system resulted exhibits a red shift of absorption and fluorescence upon heating. Because we condensed the fluorescence group with SMA, the copolymer of styrene and maleic anhydride containing pendent 1,8-naphthalimide moiety would be promising solid-state fluorescent materials. And styrene in the system is employed as diluent.[13] We changed the styrene percentage in SMA polymer chain only to find that the fluorescent intensity of the polymers could be tuned easily with the percentage increase of styrene.

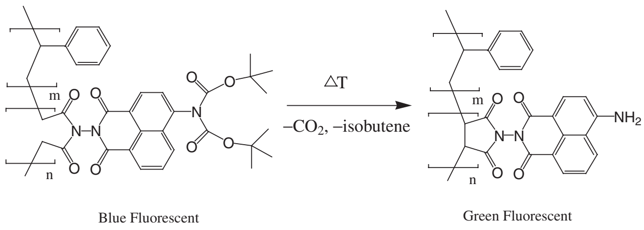

Figure 1. NTSMI thermochromic reaction with two identical fluorescent colors.

The GPC data show that the M_n, M_w, and D of SMA polymers are 4.74×10^3, 9.25×10^3 and 1.95 respectively. A mixture of *N*-amino-4-(di-*tert*-butoxycarbonyl) amino-1,8-naphthalimide[14] (1 g, 4 mmol), SMA6000 (n:$m = 1$:6) (1.45 g, 2 mmol), 4-dimethylaminopyridine (30 mg, 0.3 mmol) and anhydrous THF (20 mL) was stirred and heated under reflux under argon for 24 h. Then 5 mL of acetic anhydride was added. And the mixture was heated under reflux for 1 h. Then the reaction mixture was cooled and filtered. The filtrate was poured into 400 mL of alcohol to separate out light yellow solid. Then the solid was washed by alcohol at 60 °C until the UV absorption of the compound can not be testified in the alcohol. Then the solid was dried under vacuum to obtain 1.4 g (NTSMI) in 78% yield. The pendent concentration of the amino-1,8-naphthalimide in copolymer NTSMI is 21.6% determined by UV–vis absorption, which is also confirmed by ^{1}H NMR spectra. The T_g of NTSMI was measured to be 145 °C.

After heat treatment NTSMI changed its color and emited green fluorescence. This shows that the decomposition process should be as shown in Figure 1. The stimulated data from HyperChem software shows that the bond length between N atom at 4-position of naphthalimide and C atom linked to it is longer than the bond length between this C atom and the O atom in carbonyl. It means the C–N bond is more easily to break than C–O bond. So it leads to the fact that after NTSMI is heated, the color of copolymer becomes deeper and the fluorescence changes from blue to green. At the same time, the solubility of NTSMI decreases much after the decomposition because of the thermal cleavage of *tert*-butyl groups.

Figure 2 shows that the absorption spectra of NTSMI change greatly after its solid film is heated. The absorption at 350 nm at room temperature is red shifted and wider after it is heated. And the color of the compound becomes deeper from light yellowish white to reddish orange. This shows that the decomposition pro-

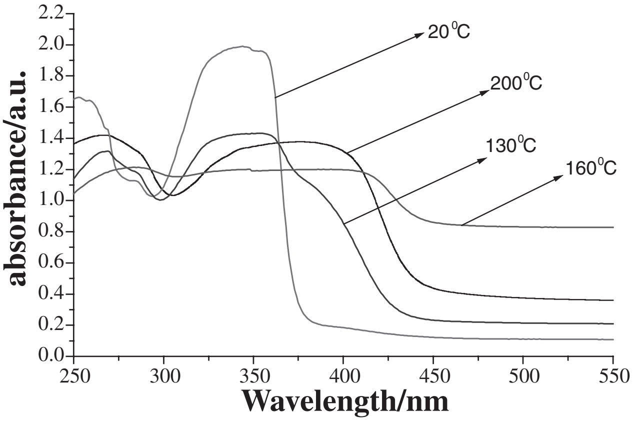

Figure 2. The absorption spectral changes of NTSMI in film when heated.

cess to break C–N bond of the di-*tert*-butoxycarbonyl substitute should begin at temperature of 110 °C.

At the initial heating step, the two C–N bonds linked to the N atom on the 4-position of naphthalimide are very easy to break and change into an amino group, which increases the electron-donating ability on the 4-position of naphthalimide. At the same time, the electron-donating direction of the amino group on 4-position is in consistency with that of carbonyl on the 1,8-position so that the fluorescent intensity has been greatly increased. The fluorescent emission would shift to longer wavelengths, i.e. it emits a green color light. However, the amino group of NTSMI would be easily oxidized becoming a nitroso group after heated in air. So the fluorescent intensity is soon decreased because nitroso group is strongly electron-withdrawing. Because of this chemical modification, we can anticipate that with the increasing of temperature, di-*tert*-butoxycarbonyl amino group on the 4-position first changes to amino group and then to nitroso group, which can well explain the phenomenon that the fluorescence of NTSMI first becomes stronger and then very weaker with the increasing of temperature as shown in Figure 3.[15] Its fluorescence maximum wavelength is red shifted about 68 nm from 463 nm at 20 °C. The fluorescent color changes apparently and the fluorescence increases much suddenly at 110 °C. The red shift of maximum wavelength at 110 °C shows that at this temperature large amount of NTSMI begins to decompose, and decompose entirely at about 160 °C. The decreasing of fluorescence begining from 170 °C may be caused by the oxidation of amino group at 4-position of naphthalimide after heated in air. When the solid film is heated to 190 °C, it appears no or very weak fluorescence, which means most of amino group on the 4-position has become nitroso group after the oxidation. The copolymer undergoes an irreversible change from a photostable primary color and emission light to a photostable secondary color and emission light at meantime.

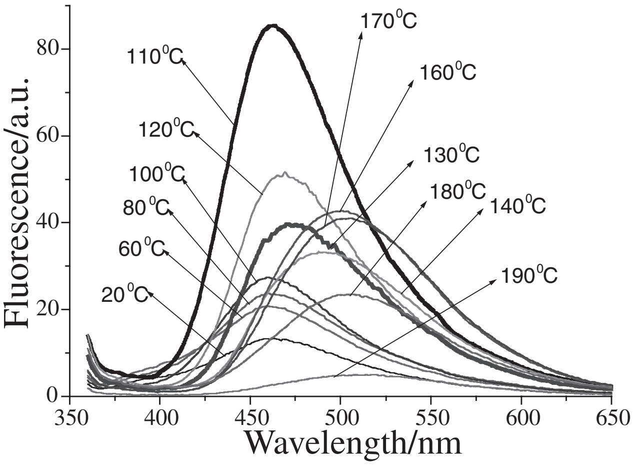

Figure 3. The fluorescent spectral changes of NTSMI in film when heated.

The color including emission peak of 1,8-naphthalimide is dependent on the presence of a strong electron-donating substitute linked to the 4-position of the naphthalimide ring.[12,16] If the masking and protecting group such as di-*tert*-butoxycarbonyl is thermally cleaved, an electron-donating, heat-sensitive NH_2 group can be achieved from (di-*tert*-butoxycarbonyl) amino group, the fluorescence of the naphthalimide fluorophore drastically enhanced and red-shift obviously. The parent primary amino-functionalized copolymer is regenerated in almost quantitative yield by elimination of an alkene and carbon dioxide.

In summary, a simple concise, low cost and efficient method to synthesize a new class of thermochromic and fluorescent NTSMI copolymers based on copoly(styrene-maleic anhydride) (SMA) and amino-substituted 1,8-naphthalimide were described. NTSMI copolymers synthesized herein show solid state fluorescence emission, the color and fluorescence of them would be changed by heat. These would be very promising functional materials for various applications such as thermopaint, optical data storage and printing materials, laser-mark and so on.

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14 4-(di-tert-butoxycarbonyl) amino-1,8-naphthalic anhydride (purified by silica gel column chromatography) mp >250 °C. ^{1}H NMR (500 MHz, Bruker, relative to TMS, $CDCl_3$) $\delta = 1.65$(s, 18H, CH_3), 7.85(m, 1H, naphthalic H), 8.3(d, 1H, naphthalic H, $J = 8.56$), 8.55(d, 1H, naphthalic H, $J = 8.38$), 8.6(d, 1H, naphthalic H, $J = 8.34$), 8.64(d, 1H, naphthalic H, $J = 7.28$). Mass spectra were obtained with HP5989A, Mariner API time of flight (TOF, TIS ion source, PE Corp.) and API2000 (TIS, PE Corp.) spectrometers. Infrared spectra were measured on a Nicolet Magna IR550. UV-vis-NIR spectra were recorded on a Varian Cary500. Fluorescence spectrum was recorded on a Varian Cary eclipse fluorescence spectrophotometer. Quinoline was distilled over calcium hydride. SMA series were donated by SARTOMER Co. Inc. (ATOFINA) Shanghai Office.
15 The temperature in Figure 3 is increased regularly and all temperature points are kept constant for 5 minutes. While the decomposition and oxidation of the group on the 4-position of naphthalimide depend on not only the temperature changes but also the heating time. All maximum fluorescent wavelengths at different temperatures lower than 110 °C or higher than 160 °C are similar. While the fluorescence is red shifted greatly from 110 °C to 160 °C, which shows that the animo group is easily to be produced on the 4-position of naphthalimide during this temperature range. All fluorescent intensity at different temperatures higher than 160 °C decreases quickly, which shows that the amino group on the 4-position is easy to become nitroso group at the temperature higher than 160 °C. In summary, the longer the heating time within the temperature range from 110 °C to 160 °C, the more quickly the fluorescence red shifted. While to the situation when the temperature is higher than 160 °C, the longer the heating time, the more quickly the fluorescence intensity decreases.
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