

Reversible Thermal-Induced Fluorescence Color Change of Tetraphenylethylene-Labeled Nylon-6

Jiaru Xu, Wenxi Ji, Chao Li, Yufeng Lv, Zijie Qiu, Longcheng Gao,* Erqiang Chen, Jacky W. Y. Lam, Benzong Tang, and Lei Jiang

Nylon is the first synthetic fiber material and is widely used throughout the world. However, traditional nylons show limited optical applications as they emit no or weak fluorescence. Herein, a fluorescent nylon-6 is synthesized by utilizing tetraphenylethylene (TPE) carrying two amino groups as coinitiator. The resulting TPE-labeled nylon-6 exhibits reversible thermal-induced fluorescence color change. This unique property arises from the synergistic effect of its chemical structure and conformation. The thermal expansion of the polymer at high temperature induces the phenyl rings of TPE to rotate in a greater extent, which decreases the conjugation of TPE to lead to a blueshift in its fluorescence. The novel fluorescence property of TPE-labeled nylon-6 enables it to find applications in fields like chemosensor and security label.

Nylon has been used throughout the world as an important synthetic fiber and engineering plastic because of its excellent mechanical and thermal stability derived from the extensive hydrogen bonds between the nylon chains.^[1] For example, nylon-6 is one of the prominent members of the nylon families with the characteristics of toughness, high tensile strength, and elasticity. Nylon-6 has been widely used in automotive, textile, and package areas.^[2,3] However, due to the lack of strong chromophoric groups, traditional nylons generally show no or weak fluorescence and thus have found limited optical applications.

Fluorescent materials have received continued interest due to their wide applications in areas such as mechanochromism,^[4–7] bioimaging,^[8,9] and chemosensing.^[10–12] Introduction of fluorescent dyes to nylon chains can generate emissive polymers with high-technological applications. For example,

chromophore-immobilized nylon membranes have been applied to detect toxic chemical compounds at ultratrace level by fluorescence measurements.^[13,14] K⁺-selective film sensors were fabricated by introducing electrically charged solvatochromic dyes into nylon films. The fluorescence response to K⁺ possesses the features of excellent selectivity and fast rate.^[15] However, the postmodifications often suffer from incomplete functionalization, poor miscibility, or weak stability.

Herein, we prepared fluorescent nylon-6 by using tetraphenylethylene (TPE), a typical aggregation-induced emission luminogen,^[16,17] carrying two amino

functionalities as coinitiator. The synthetic procedure is fully adapted to the traditional nylon-6 polymerization. The resulting polymer, named TPE-labeled nylon-6, exhibits unique fluorescence property. Its fluorescence color can be tuned by controlling the intramolecular rotation of the TPE's phenyl rings. Nylon-6 is a semicrystalline polymer. During its melting transition at high temperature, the movement of the nylon chain will interfere the intramolecular motion of TPE to induce fluorescence change of the chromophoric unit.^[18–20]

TPE-labeled nylon-6 was synthesized by ring-opening polymerization of caprolactam in the presence of 1,2-bis(4-aminophenyl)-1,2-diphenyl ethylene (**1**) as coinitiator (Scheme 1). Since the amount of compound **1** used is tiny, the polymerization efficiency will not be affected. The synthetic procedure is suitable for industrial production. The ¹H NMR spectrum of the obtained polymer shows characteristic

Dr. J. R. Xu, C. Li, Y. F. Lv, Prof. L. C. Gao, Prof. L. Jiang
Key Laboratory of Bio-Inspired Smart Interfacial Science
and Technology of Ministry of Education
Beijing Key Laboratory of Bio-inspired Energy Materials and Devices
School of Chemistry
Beihang University
Beijing 100191, P. R. China
E-mail: lcgao@buaa.edu.cn

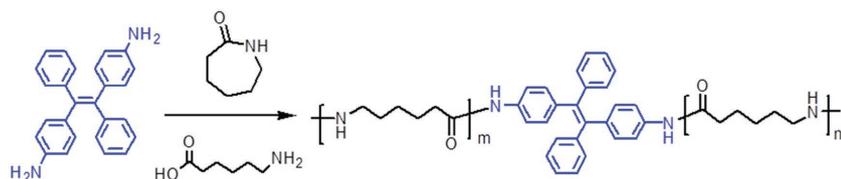
Dr. J. R. Xu, Prof. E. Q. Chen
Beijing National Laboratory for Molecular Sciences
Key Laboratory of Polymer Chemistry and Physics of Ministry of Education
Center for Soft Matter Science and Engineering, College of Chemistry
Peking University
Beijing 100871, P. R. China

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adom.201701149>.

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Dr. W. X. Ji
Beijing Research Institute of Chemical Industry
China Petroleum & Chemical Corporation
Beijing 100013, P. R. China

Dr. Z. J. Qiu, Dr. J. W. Y. Lam, Prof. B. Z. Tang
Department of Chemistry
Hong Kong Branch of Chinese National Engineering Research
Center for Tissue Restoration and Reconstruction
Institute of Molecular Functional Materials
State Key Laboratory of Nanoscience
Division of Biomedical Engineering and Division of Life Science
The Hong Kong University of Science and Technology
Clear Water Bay, Kowloon, Hong Kong 999077, P. R. China



Scheme 1. Synthetic route to TPE-labeled nylon-6.

resonance signals of the methylene protons and the amide proton of nylon-6 (Figure S1, Supporting Information). Besides, those peaks at δ 7.0 are associated with the phenyl proton resonances of TPE. The calculated weight fraction of TPE was about 0.4%, and was slightly higher than the feed ratio, suggesting high reactivity of compound 1. The viscosity average molecular weight of TPE-labeled nylon-6 was determined to be \approx 23 000 by the viscosity method. The polymer exhibits not only good solubility, but also good mechanical strength as shown in Figure S2 in the Supporting Information. The sample showed excellent thermal stability. As shown in Figure S3 in the Supporting Information, the 5% loss temperature was above 350 °C.

Figure 1A shows the fluorescence spectra of TPE-labeled nylon-6 at various temperatures. At low temperature,

TPE-labeled nylon-6 emits a strong blue light at 485 nm. The fluorescence intensity becomes lower with an increase in temperature. Above 120 °C, the emission starts to blueshift (Figure 1B), and the fluorescence intensity changes little even further heating is applied. Clearly, the introduction of TPE to the nylon-6 chain has endowed it with strong light emission. It is noteworthy that

the emission intensity at 190 °C is still strong, making the TPE-labeled nylon-6 to find potential high-temperature fluorescent applications.

Such phenomenon was not observed in the blend system. We doped nylon-6 with the same amount of TPE. From the fluorescence spectra of the polymer/dye mixture measured at different temperatures (Figure 1C), we found that the peak maximum was all located at the same wavelength and no obvious fluorescence color change was observed. On the other hand, the fluorescence intensity decreases in a much faster extent than that of the dye-labeled one. The emission of TPE-doped nylon-6 is almost quenched completely at 180 °C. This result suggests that TPE-doped nylon-6 exhibits the conventional thermal-induced fluorescence decay but shows no phenomenon of thermal-induced fluorescent color change.

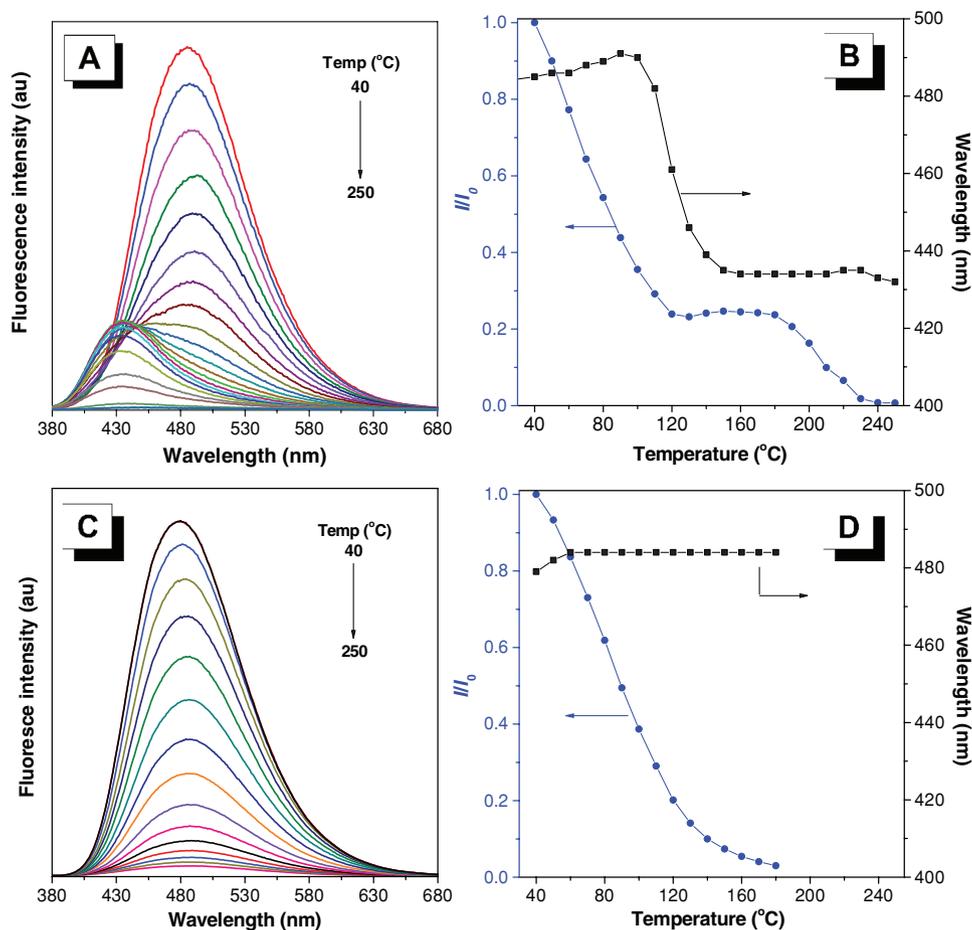


Figure 1. Fluorescence spectra of A) TPE-labeled nylon-6 and C) TPE-doped nylon-6 at different temperatures. Plots of relative fluorescence intensity (I/I_0) and emission wavelength of B) TPE-labeled nylon-6 and D) TPE-doped nylon-6 versus temperature, where I_0 is fluorescence intensity at 40 °C.

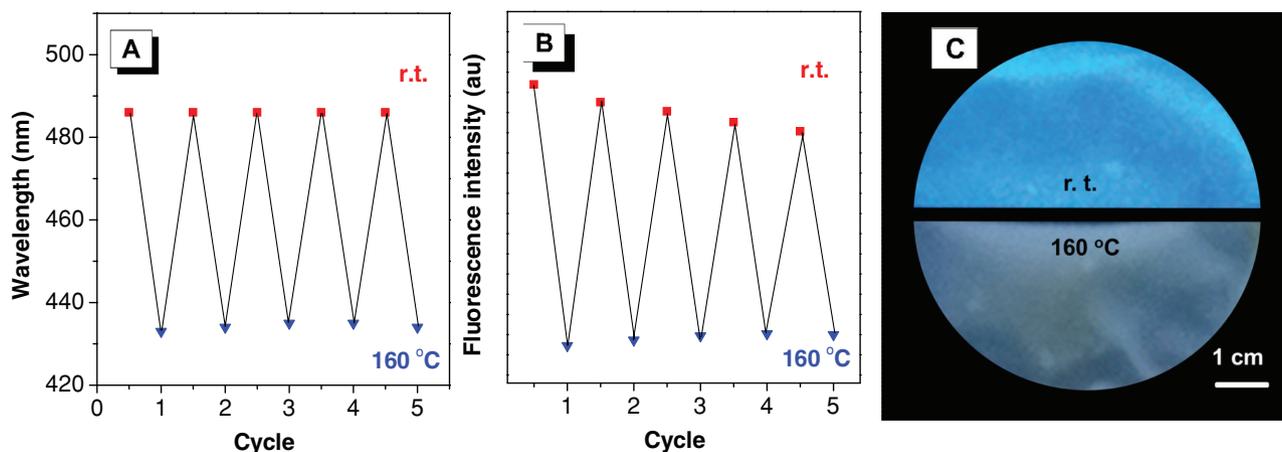


Figure 2. Reversibly switching of the A) emission maximum and B) fluorescence intensity of TPE-labeled nylon-6 at room temperature and 160 °C by repeated heating and cooling cycle. C) Fluorescence photographs of the TPE-labeled nylon-6 at room temperature and 160 °C.

We repeated the fluorescence measurement of TPE-labeled nylon-6 at room temperature and 160 °C for several times, and found that the fluorescence maximum switches between ≈ 485 and 432 nm with excellent reversibility. The fluorescence intensity also changes from strong to weak and vice versa by repeatedly heating and cooling cycle (Figure 2B). The fluorescence properties of TPE-containing (co)polymers are strongly dependent on the polymeric matrix. For example, the fluorescence of TPE-incorporated thermoplastics exerts dramatic change only when the glass transition temperature of the polymers is reached.^[21–24] The high melting point of nylon-6 widens the temperature window of its dye-labeled form to exhibit strong light emission. On the other hand, the reversible thermal-induced fluorescence color change indicates that the present system possesses a high stability, as confirmed by the fluorescence photographs of the TPE-labeled nylon-6 at room temperature and high temperature (Figure 2C). All these make TPE-labeled nylon-6 to serve as a high-temperature functional material.

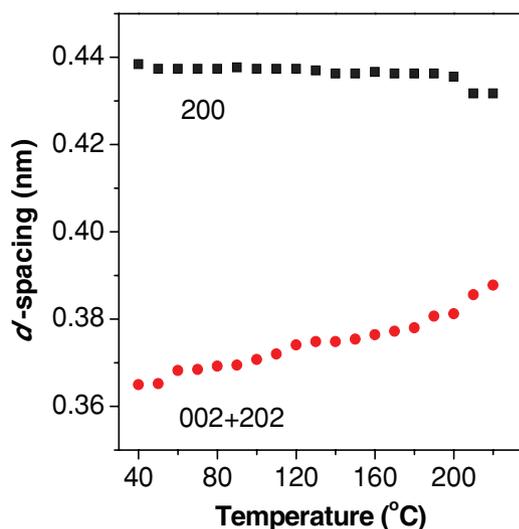


Figure 3. Change of d spacings of the (200), (002), and (202) reflection peaks with temperature.

In order to get insight into such emission switching behavior, wide-angle X-ray diffraction (WAXD) was employed to study the thermal behavior of the sample. As shown in Figure S4 in the Supporting Information, at room temperature, two typical diffraction peaks of monoclinic α phase are observed at 20° and 24.5° and indexed as (200) and (002), respectively. The (200) plane is related to the a axis length of the unit cell, which is also the distance between the hydrogen-bonded nylon chain sheets. The (002) plane corresponds to the c axis length. Upon heating, the (200) and (002) reflection peaks move closer to each other. From the plot of d spacing against temperature (Figure 3B), we can see that the d spacing of the (200) peak changes little with temperature, while that of (002) becomes higher at high temperature. This suggests the occurrence of anisotropic thermal expansion in the unit cell. The strong hydrogen bonding maintains the a axis length unchanged. Two transitions occur at ≈ 120 and 220 °C on the c axis. The later one is associated with the melting of nylon-6, as confirmed by the differential scanning calorimeter (DSC) result (Figure S5, Supporting Information). The former one on the other hand results from the chain expansion perpendicular to the hydrogen-bonded chain sheet or α to α' transition or Brill transition.^[19] This transition was usually interpreted by the disordered conformation of the methylene sequences and the pseudo-hexagonal packing of the molecular chains. However, the hydrogen bonds were still preserved even at high temperatures.^[25,26]

From the WAXD results, we can see that the tiny amounts of TPE molecules affect little the crystal structure of nylon-6 and they should be dispersed in the amorphous domains. Similar to the crystalline phase, intensive hydrogen bonds exist in the amorphous phase even at high temperature. At low temperature, the hydrogen-bond-locked matrix restricts the intramolecular rotations of all the phenyl rings of TPE. When heated above the transition temperature, the chains expand, providing sufficient space for the intramolecular rotations of TPE. It is worth to note that the phenyl rings of TPE connected to the nylon chains are still restricted to undergo rotation, while the other two can rotate freely. Overall, the conjugation of TPE decreases to cause emission blueshift. Such unique properties

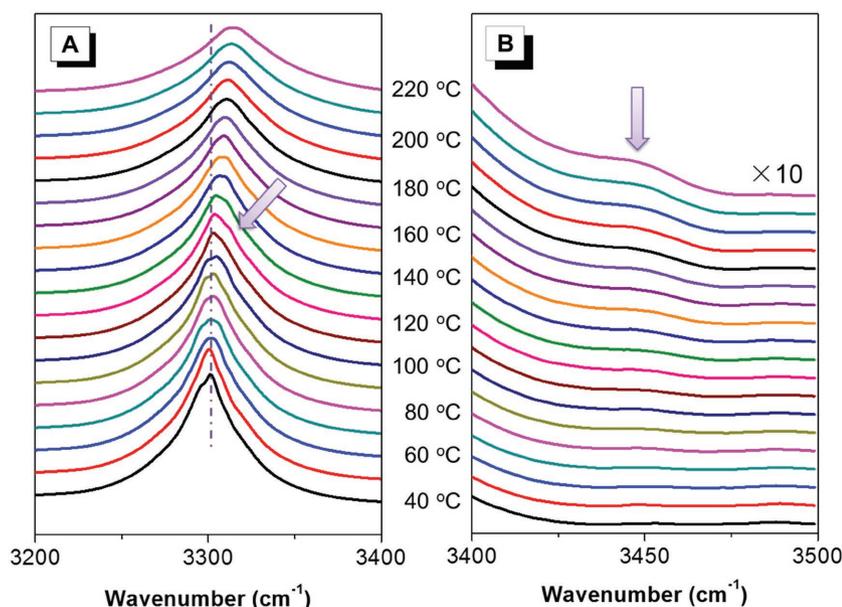


Figure 4. FTIR spectra of TPE-labeled nylon-6 at 3200–3450 cm^{-1} obtained by heating the sample from 40 to 220 °C. A) A shoulder appears at higher wavenumber at 120 °C, indicating the decrease in hydrogen-bonding strength. B) A small peak appears at 3450 cm^{-1} above 120 °C, indicating the disassociation of the hydrogen-bonded N–H groups.

arise from the synergistic effect of the chemical structure and the conformation of TPE-labeled nylon-6.

The conformational transition of nylon-6 is strongly influenced by hydrogen bonds, as confirmed by in situ variable temperature Fourier transform infrared (FTIR) spectroscopy. **Figure 4** shows the spectra in the region of 3200–3500 cm^{-1} from 40 to 220 °C. The band at around 3300 cm^{-1} is assigned to the hydrogen-bonded N–H stretching band, while the band at 3450 cm^{-1} is related to free N–H stretching vibration.^[27] As the N–H stretching band is not sensitive to conformation, this peak arises from both the crystalline phase and the amorphous phase.^[28,29] At room temperature, all the N–H groups are hydrogen bonded. Above 120 °C, the hydrogen-bonded N–H stretching band shifts to higher frequency and exhibits a steady increase in bandwidth with a lower intensity, indicating that the bond strength becomes weaker. Meanwhile, a small broad peak starts to be detected at 3440 cm^{-1} at 120 °C, implying the presence of free N–H groups. Such transition is confirmed by the dynamic mechanical analysis. As shown in Figure S6 in the Supporting Information, the TPE-labeled nylon-6 displays one obvious transition of the tan Delta peak at around 107 °C. These are in accordance with the volume expansion between nylon chains, which induces rotation of the free phenyl rings of TPE to cause the fluorescence change.

Figure 5 shows the schematic principle of fluorescence color change of TPE-labeled nylon-6 induced by heating. Due to their low polarity and large size, the TPE moieties are

excluded from the crystalline regions and entered the amorphous phases. In order to facilitate the description of the transition process, we drew the TPE-containing microregion with the polymer chain in vertical direction. Similar to the crystalline phase, strong hydrogen bonds exist between the polymer chains in the amorphous region. At low temperature, the rotations of all the phenyl rings of TPE are restricted in the nylon-6 matrix. As the temperature rises, the segmental motions of nylon-6 chains are activated and the volume between the polymer chains expands, providing sufficient space for the intramolecular rotation of the free phenyl rings. However, the phenyl rings chemically connected to the nylon-6 chains are still restricted unless chain diffusion occurs at above the melting point. The conjugation of the chromophoric group decreases to cause blueshift in the emission. When the temperature increases above the melting point, the chain diffusion is totally motivated, which sequentially activates the rotation of all the phenyl rings of TPE to completely quench its light emission.

In conclusion, we synthesized a luminescent nylon-6 by the addition of a small amount of diamino-functionalized TPE during the traditional ring-opening polymerization of caprolactam. The TPE units are covalently bonded in the nylon chains and exhibit a reversible thermal-induced fluorescence color change. Such phenomenon is due to the fact that the polymer chain undergoes Brill transition upon heating. During this process, the hydrogen bonds between the nylon-6 began to disassociate. The interchain space becomes bigger, providing

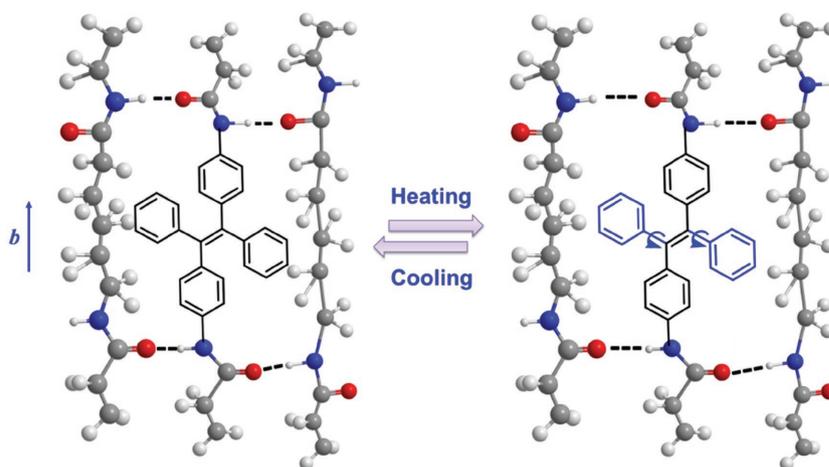


Figure 5. Schematic representation of the TPE-labeled nylon-6 exhibiting reversible thermal-induced fluorescence color change. At low temperature, the rotations of all the phenyl rings of TPE are restricted to endow the material with strong fluorescence. When temperature increases, the chains expand, providing sufficient space for the rotation of the free phenyl rings. The connected phenyl rings are still restricted to undergo rotation unless the melting point of the polymer is reached. Overall, the conjugation of TPE decreases to result in blueshift in the fluorescence.

sufficient space for the intramolecular rotation of the free phenyl rings of TPE. The conjugation of TPE reduces, leading to a blueshift in the emission. Thus, this material may help to enlarge the usage of stimuli-responsive polymers in real-world application and may apply as antifake labels and indicators of temperature.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

fluorescence, nylon-6, tetraphenylethylene

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