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The thermoresponsive behaviour of a poly(*N*-isopropylacrylamide) hydrogel with a D-π-A type pyran-based fluorescent dye

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ABSTRACT

A thermoresponsive poly(NIPAM-co-fluorophore) hydrogel labeled with pyran-based fluorescent dye was prepared using conventional radical copolymerization. The low critical solution temperature behaviour was investigated using UV–vis spectroscopy which allowed the measurement of the phase transition over a wide range of temperature. The poly(NIPAM-co-fluorophore) in aqueous solution underwent a phase transition at 36–58 °C. The fluorescence intensities of the polymer in aqueous solution increased with increasing temperature across the low critical solution temperature transition range. The fluorophore displayed a blue shift in emission with increase in temperature due to destabilization of the excited state. Evidence from fluorescence and dynamic light scattering demonstrated that, >58 °C, the size of the polymer aggregates was 12,500 m. The morphology of the internal microstructure of the poly(NIPAM-co-fluorophore) hydrogel was observed using scanning electron microscopy.

1. Introduction

Temperature-responsive polymers and hydrogels have gained scientific and technological importance and the characteristics of these materials have been studied extensively for applications such as drug delivery, fluorescent thermometer and separation systems [1–4]. One of the most intensively studied polymers in this field is poly(*N*-isopropylacrylamide) (PNIPAM) which exhibits a low critical solution temperature (LCST) transition from 30 to 45 °C [5,6]. The polymer is hydrophilic and soluble in water < LCST but becomes hydrophobic and forms a macroscopic coacervate phase above that temperature, owing to the fluctuation of hydrophobic interactions and hydrogen bonding [7]. This phase transition is accompanied by a release of water bound to the polymer chain, which is an endothermic process. In previous papers [8,9], we have reported bistable photoswitching in poly(*N*-isopropylacrylamide) using a photochromic spironaphthoxazine hydrogel for optical data storage. Some copolymers with fluorophore have been reported [10–15], in which the fluorescence intensity of the fluorophores was controlled by temperature as external stimuli. To the best of our knowledge, there are no reports of PNIPAM copolymers with electron donor-π-conjugate-electron acceptor (D-π-A) type fluorophores. D-π-A type pyran-based fluorescent dyes such as 4-(dicyanomethylene)-2-methyl-6-(*p*-(dimethylamino)styryl)-4*H*-pyran (DCM) have been intensively developed for applications as photo- and electroluminescent materials in the fields of dye lasers [16], sensors [17] and dye-sensitized solar cells [18]. Their fluorescence properties are highly sensitive to changes in external environment such as polarity and pH because of their intrinsic intramolecular charge transfer character [19,20]. Previous work [21] by the present research group reported the synthesis, photophysical properties and unusual aggregation-induced fluorescence changes in some a novel pyran-based fluorophore copolymer. This paper concerns fluorescence-based investigations of the thermoresponsive behaviour of a poly(*N*-isopropylacrylamide) hydrogel with D-π-A type pyran-based fluorescent dye.

2. Experimental

Melting points were determined using Electrothermal IA 900 apparatus and were uncorrected. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer using an electron energy of 70 eV and the direct probe EI method. ^{1}H NMR spectra was recorded in $CDCl_3$ using a Varian Inova 400 MHz FT NMR Spectrometer using TMS as internal standard. The weight-average molecular weight

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(Mn) and polydispersity (Mw/Mn) of the polymer was measured on a PL-GPC model 210 chromatograph at 25 °C using THF as the eluent and standard polystyrene as the reference. Fluorescence spectra were measured on a Shimadzu RF-5301PC Fluorescence spectrophotometer. The UV–vis spectra and transmittance were obtained on an Agilent 8457 UV–vis spectrophotometer. The LCST values were also determined by spectrophotometric detection of the changes in transmittance ($\lambda_{max} = 300$ nm) of aqueous polymer solutions heated at a constant rate (0.2 °C min^{-1}) with a thermostatically controlled cuvette. Dynamic light scattering (DLS) measurements was carried out on a Wyatt Technology Dynapro Titan instrument at fixed with the 828.6 nm line of a laser as excitation source.

2.1. Materials

2,6-Dimethylpyran-4-pyrone, allyl cyanoacetate and 4-(diphenylamino)benzaldehyde were purchased from Aldrich. *N*-Isopropylacrylamide (Aldrich) was purified by recrystallization from a mixture of toluene/hexane (1/4) and dried in vacuum. 2,2′-Azobis-(isobutyronitrile) (AIBN) was recrystallized from methanol. The other chemicals were of the highest grade available and were used without further purification. All employed solvents were analytically pure and were employed without any further drying or purification.

2.2. Synthesis of monomer ***5***

2.2.1. Allyl-cyano-2-(2,6-dimethyl-4H-pyran-4-ylidene)acetate ***3***

A mixture of 2,6-dimethylpyran-4-pyrone (3 g, 24 mmol) **1**, allyl cyanoacetate **2**, (3 g, 24 mmol), and acetic acid (12.5 ml) was refluxed for 24 h. The crude solid obtained was filtered, washed with methanol, and recrystallized from methanol several times. Yield: 32%; mass (m/z) 231 (M^+). ^{1}H NMR (400MHz, $CDCl_3$): δ 2.27 (s, 6H), 4.65 (d, 2H), 5.20(d, 1H), 5.36 (d, 1H), 5.94 (m, 1H), 6.59 (s, 1H), 7.87 (s, 1H). EA: Anal. calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.17; H, 5.72; N, 6.03%.

2.2.2. Allyl-2-(2,6-bis((E)-4-(diphenylamino)styryl)-4H-pyran-4-ylidene)-2-cyanoacetate ***5***

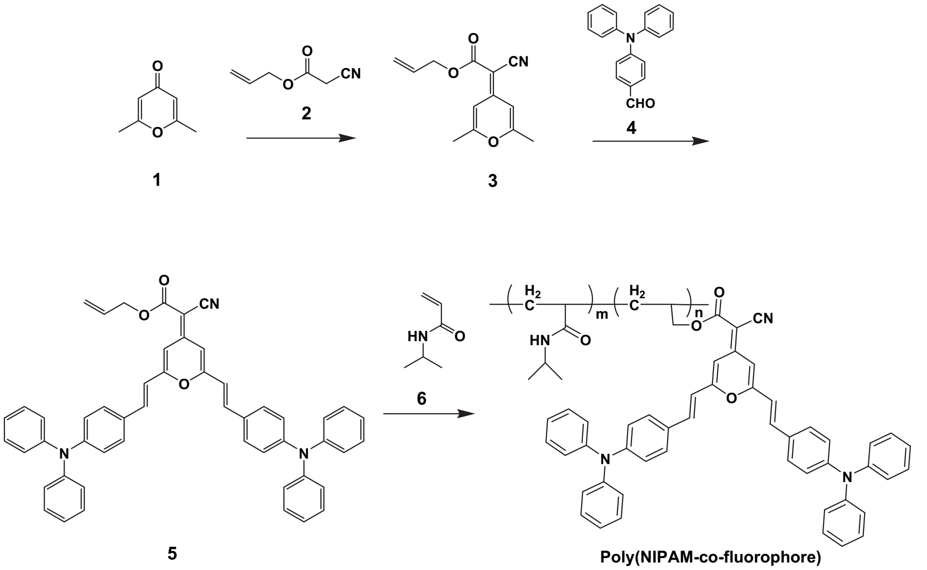
A solution of allyl-2-cyano-2-(2,6-dimethyl-4H-pyran-4-ylidene)acetate **3** (1 g, 4.3 mmol), 4-(diphenylamino)benzaldehyde **4** (1.4 g, 5.2 mmol), and piperidine (0.3 ml) in 1-propane (50 ml) was refluxed for 24 h using Dean–Stark trap. The ensuing solution was cooled to room temperature and the solid product was isolated and washed well with 1-propanol and then dried. The reaction mixture was evaporated to remove solvent and separated by column chromatography using chloroform. Yield: 30%; mp 229–231 °C; mass (m/z) 741 (M^+). ^{1}H NMR (400MHz, $CDCl_3$): δ 4.69 (dt, $J = 1.48$ Hz, 2H), 5.23 (dd, $J = 3.96$ Hz, 1H), 5.37 (dd, $J = 4.64$ Hz, 1H), 5.94 (m, 1H), 6.60 (d, $J = 6.44$ Hz, 1H), 6.64 (d, $J = 6.36$ Hz, 1H), 6.73 (s, 1H), 7.02 (m, 30H), 8.04 (s, 1H). EA: Anal. calcd for $C_{51}H_{39}N_3O_3$: C, 82.57; H, 5.66; N, 5.30. Found: C, 81.84; H, 5.78; N, 5.44%.

2.3. Synthesis of poly(NIPAM-co-fluorophore)

N-Isopropylacrylamide **6** (2.26 g, 20 mmol), allyl-2-(2,6-bis((E)-4-(diphenylamino)styryl)-4H-pyran-4-ylidene)-2-cyanoacetate **5** (0.15 g, 0.2 mmol), and 2,2′-azobis-(isobutyronitrile) (0.032 g, 0.2 mmol) were dissolved in anhydrous THF (20 ml) under dry N_2. After being heated for 3 days at 65 °C, the resultant mixture was precipitated from ether. The ensuing polymer was dried in vacuum to give satisfactory yield as orange-colored powder. Yield: 85%; Gel permeation chromatography (GPC): Mn: 21,733, Mw: 25,342, MP: 28,225, Mw/Mn: 1.16.

3. Results and discussion

The organic functional dyes with D-π-A charge transfer are the most important class of compounds for elucidating the relationships between push-pull chromophores and their optical properties [22]. Despite the broad application of these and other D-π-A chromophores [23,24] for the elucidation of reaction rates, chemical equilibria, nonlinear optical properties, and so on, accurately explaining the relationship between substituted groups and optical properties remains the subject of active debate [25]. The synthetic route of an monomer **5** and poly(NIPAM-co-fluorophore) is depicted in Scheme 1. We designed a new D-π-A charge transfer dye **5**,



Scheme 1. Synthesis of a D-π-A charge transfer dye, **5**, and poly(NIPAM-co-fluorophore).