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A chromophore-labeled poly(*N*-propargylamide): a new strategy for a stimuli-responsive conjugated polymer

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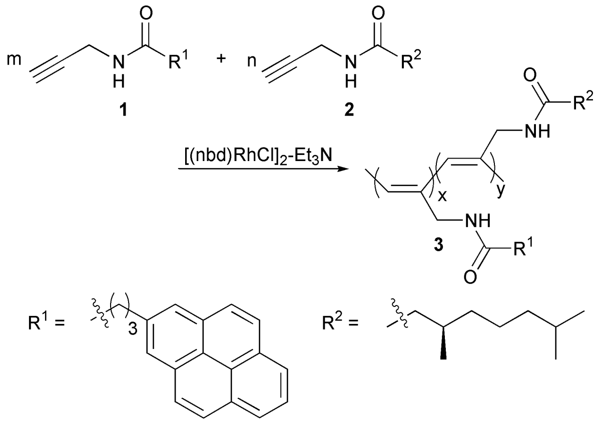
A new stimuli-responsive conjugated polymer was synthesized, where, following the change of secondary conformation from helical to disordered state, the fluorescence property of the side chain chromophore changes upon sensing external stimuli.

Stimuli-responsive conjugated polymers have gathered much attention because they are potentially superior as sensors to small molecules in responsiveness to a very minor perturbation.[1] The output upon sensing external stimuli always utilizes a change in properties of the polymer. In most cases, the change in polymer property originates from a change of the degree of the main-chain conjugation, *i.e.*, planarity of the main chain. Here, we report a new stimuli-responsive conjugated polymer, in which the change in external environment results in a reversible change in the secondary conformation between the helix and random coil, leading to a change in fluorescence property of the side-chain chromophore.

We used, in the present study, a stereoregular (*cis*) poly(*N*-propargylamide), prepared with a Rh catalyst, as a framework based on the following strategy (Scheme 1). The Rh-based poly(*N*-propargylamides) are able to construct well-arranged intramolecular hydrogen bonds between the side chains.[2] The hydrogen bonds rigidify the polymer backbone and simultaneously promote the main chain to self-organize into a helical conformation. In other words, like α-helical polypeptides, the helical conformation of poly(*N*-propargylamides) is biomimetically stabilized by means of intramolecular hydrogen bonding. The helical conformation is, however, readily deformed into a randomly coiled state, when the intramolecular hydrogen bond is cleaved by external stimuli such as heating or adding polar additives.[3] Interestingly, the thermally induced conformational change occurs in a quite narrow temperature range (15–30 °C) because the random coil–to–helix transition of poly(*N*-propargylamides) involves very large negative entropy and enthalpy changes.[3] This excellent stimuli-responsiveness means that the rigidity of the backbone drastically changes upon a change in temperature and/or in solvent composition. For example, in the case of poly(*N*-propargylhexanamide) ($R^1 = R^2 = n\text{-}C_5H_{11}$ in Scheme 1), the viscosity index (α) in the Mark–Hauwink–Sakurada plot, which is an indication of the backbone rigidity, steeply decreases from 0.98 (a semiflexible chain) to 0.76 (a flexible chain) upon a very small temperature change from 30 to 40 °C.[2,3] It is, thus, expected that, if chromophores are incorporated into the side chain, the helical state possesses low population of the excimer forming site due to the limited mobility of the polymer chain,[4] whereas a stimuli-induced deformation results in an increase in the probability of the excimer. The change in the population of the excimer forming site consequently influences the fluorescence property of the chromophores.

An *N*-propargylamide having a pyrene chromophore (**1**) was employed as a monomer (Scheme 1). Since the homopolymerization of **1** gave an insoluble polymer, the copolymerization with a chiral comonomer, (*R*)-*N*-propargyl-3,7-dimethyloctanamide (**2**), was carried out. The copolymerization (**1**:**2** = 30:70 in feed), catalyzed with $[(nbd)RhCl]_2$–Et_3N† in $CHCl_3$, gave the copolymer (**3**) in 90% yield as a methanol-insoluble part. The number- and weight-average molecular weights were estimated by GPC (polystyrene calibration) to be 26100 and 42000, respectively. The copolymer composition (*x*:*y*) determined using ^{1}H NMR was 41:59.[5]

The UV-visible spectrum of copolymer **3** is illustrated in Fig. 1. The copolymer showed an absorption attributed to the pyrene units in the range 300–370 nm in $CHCl_3$. Furthermore, a broad absorption centered at 400 nm was detected. This band around 400 nm originates from the helical conformation because the helical main chain of poly(*N*-propargylamides) without any chromophore has proven to absorb light at around 400 nm in $CHCl_3$.[3] The copolymer displayed a very large optical rotation ($[\alpha]_D = -789°$ in $CHCl_3$, $c = 0.029$ g dL^{-1}), which was opposite in sign to comonomer **2** ($[\alpha]_D = +0.25°$ in $CHCl_3$, $c = 0.41$ g dL^{-1}). The CD spectrum of the copolymer also exhibited intense Cotton effects, which were identical in shape to those of poly(**2**), in the absorption region of the main chain. All these data reveal that the copolymer adopts a helical conformation with an excess of one-handed screw sense in $CHCl_3$.



Scheme 1

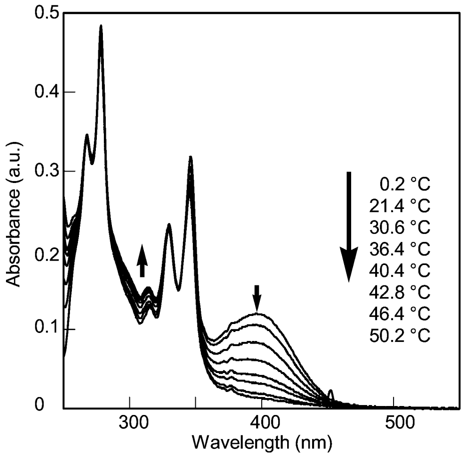


Fig. 1 Temperature variable UV-visible spectra of **3** in $CHCl_3$.

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The external-stimuli induced conformational change was first confirmed by the UV-visible spectra. In the temperature variable UV-visible spectra in $CHCl_3$ (Fig. 1), the absorption around 400 nm gradually decreased in intensity with increasing temperature, and this band cannot be detected above 45 °C. Simultaneously, the absorption around 320 nm increased in intensity. This spectral change caused a change of the color of the solution from yellow to achromatic. The change in the absorption is due to the conformational change from the helical to disordered states, which is supported by the fact that the polymers with the disordered conformation show a single absorption around 320 nm.[3] These processes were completely reversible. Thus, the copolymer readily undergoes a reversible conformational change between the helix and random coil by the thermal stimuli. The helix–to–random coil transition also took place by adding a small amount of polar solvent such as methanol: the absorption around 400 nm, which is attributed to the helical main chain chromophore, was not detected in the UV-visible spectrum of **3** in $CHCl_3$–CH_3OH (50 : 1 v/v). Thus, the conformational change is driven not only by the thermal stimuli but also by breaking the intramolecular hydrogen bond with polar solvents.

The change of the secondary conformation of **3**, induced by the external stimuli, led not only to a change in the main-chain absorption but also the fluorescence property of the side chain chromophore. In $CHCl_3$ at low temperature, that is, when the copolymer exists in the helical conformation, copolymer **3** exhibited three major emission bands around 380, 395, and 480 nm upon photoexcitation at 346 nm as shown in Fig. 2. The former two bands originate from the isolated pyrene units, and the last one is the excimer fluorescence. It is interesting that the increase in temperature increased the intensity of the excimer fluorescence, while that of the isolated pyrene unit stayed almost unchanged (Fig. 2). This means that the transition from the helix to randomly coiled conformations results in an increase in probability of excimer formation. These results indicate that population of the excimer forming site changes upon the thermally induced conformational change.

The fluorescence property also changed when the conformational change was driven by adding a polar additive: the magnitude of the excimer fluorescence was approximately two times higher in the presence of methanol compared with that in the absence of methanol (Fig. 3). Simultaneously, however, the intensity of the isolated pyrene fluorescence increased. Thus, the solvent-driven fluorescence property change appears to originate not only from an increase in the excimer population. It was confirmed that the quenching of the excited singlet state of pyrene by the main chain chromophore occurs to some degree. Therefore, the degree of the quenching by the main chain is different in the presence or absence of methanol, which means that the conformation in $CHCl_3$ at high temperature is different from that in $CHCl_3$–CH_3OH. The poor solvent, methanol, may promote the aggregation of the polymer chain to result in this conformational difference.

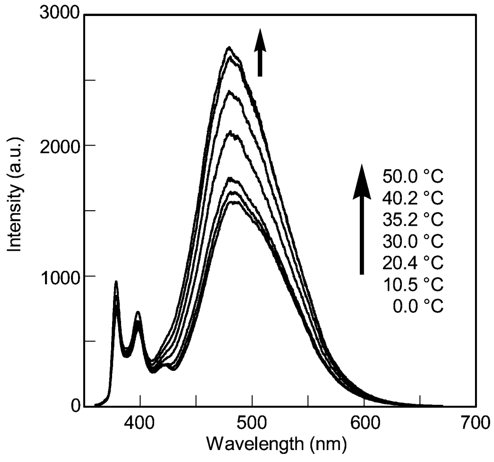

Fig. 2 Temperature variable fluorescence spectra of **3** in $CHCl_3$ (excited at 346 nm).

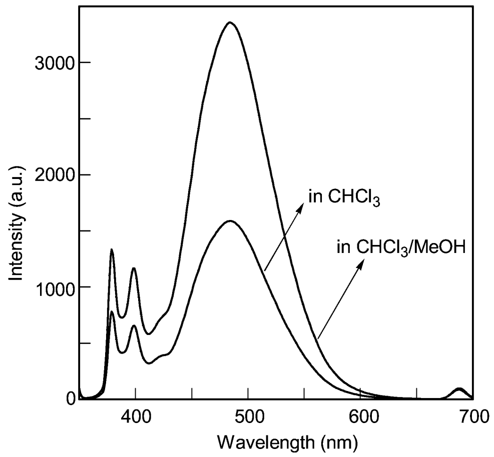

Fig. 3 Fluorescence spectra of **3** in $CHCl_3$ in the presence or absence of methanol (excited at 346 nm).

In summary, we have demonstrated a new strategy for a stimuli-responsive conjugated polymer. The produced polymer senses the variation of temperature, changes the secondary conformation and probability of excimer formation, and simultaneously outputs the change in the fluorescence property. The most characteristic feature of the present system is the very high responsiveness to the change in temperature (*ca.* 20 °C) even though the sensing utilizes a drastic conformational change occurring in the whole of the molecule. Although the mechanism is not completely understood, the polymer also senses changes in the solvent composition to result in a change of the fluorescence property. This excellent responsiveness would allow poly(*N*-propargylamides) to be applied as a new type of conjugated polymer-based sensor.

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Notes and references

† nbd = norbornadiene. The IUPAC name for norbornadiene is bicyclo-[2.2.1]hepta-2,5-diene.

1 See for recent reviews: D. T. McQuade, Q. E. Pullen and T. M. Swager, *Chem. Rev.*, 2000, **100**, 2537; and references therein.

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5 Stereoregular poly(*N*-propargylamides) show the signals attributed to vinyl and N–H protons around 6 and 8 ppm, respectively. These protons were, however, not clearly detected because of overlapping with the signals for the pyrene units. Thus, the copolymer compositions were determined by the integrated ratio of the protons for pyrene, vinyl and N–H protons to those for alkyl groups, assuming that the main-chain double bonds are quantitatively controlled to a *cis* geometry.