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Effect of alkyl chain length on thermochromic phase transition in urethane-substituted polydiacetylene crystals

Hiroaki Tachibana[a,b,*], Noriko Hosaka[c], Yoshinori Tokura[a,b,c]

[a]*Correlated Electron Research Center (CERC), 1-1-1 Higashi, Tsukuba 305-8562, Japan*
[b]*Joint Research Center for Atom Technology (JRCAT), Tsukuba 305-8562, Japan*
[c]*Department of Applied Physics, University of Tokyo, Tokyo 113-8656, Japan*

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Abstract

A series of urethane-substituted polydiacetylenes (PDA–*m*UEt) with different alkyl chain lengths ($m = 4$, 5, and 6) in side chain substituents of $(CH_2)_mOCONHC_2H_5$ were synthesized. The effect of the alkyl chain length on the thermochromic phase transition was investigated by measurements of reflectance spectra for the PDA–*m*UEt crystals. The thermochromic phase transition shows an even–odd effect for the alkyl chain length. The PDA–5UEt crystal undergoes a reversible thermochromic phase transition between A (blue) and B (red) phases, while the even-numbered PDA–*m*UEt crystal turns to the B phase on heating but does not revert completely to the initial A phase even when cooled down to room temperature. The difference in the thermochromic phase transitions of PDA–*m*UEt crystals with varying alkyl chain length was also studied by the differential scanning calorimetry (DSC).

Keywords: Urethane-substituted polydiacetylene; Thermochromism; Even–odd effect

1. Introduction

The design of supramolecular structures based on intermolecular interactions such as hydrogen bonding between urea groups and π–π interaction between mesogenic butadiyne groups has been attracting considerable interest from a viewpoint of controlling dimensionality and functionality. Interesting optoelectronic properties have been developed by utilizing such an intermolecular interaction [1–6]. One of the strategies to realize photoinduced phase transition in π-conjugated polymers is to utilize a conformation coupling between the long alkyl chain of sidegroups and the polymer backbone and to produce the first-order transition system. Based on this strategy, the introduction of the urethane groups into the sidegroups attached to polydiacetylene (PDA) backbones has provided not only an increase in solubility to common organic solvents [7,8] but also interesting physical properties such as a reversible thermochromism between the so-called A (blue) and B (red) forms [9,10]. Much work has been done on the thermochromic behavior of the urethane-substituted PDA derivatives ($(=RC{-}C{\equiv}C{-}CR=)_x$ such as poly(ETDU) ($R{=}(CH_2)_4OCONHC_2H_5$) and poly(TCDU) ($R{=}(CH_2)_4OCONHC_6H_5$) [11,12]. Recently, a photoinduced phase transition between the two phases has also been achieved in single crystals of urethane-substituted polydiacetylenes [13]. However, little is known about the role of the inner alkyl chains between urethane groups and polymer backbones in the thermochromic phase transition of the urethane-substituted PDA [14]. So far, physical properties of poly(BCMU) derivatives ($R{=}(CH_2)_nOCONHCH_2COOC_4H_9$) with various alkyl chain lengths have been reported [8,15,16], but no systematic investigation about the thermochromic phase transition has yet been undertaken for urethane-substituted PDAs. Here, we report the effect of the alkyl chain length on thermochromic behaviors for urethane-substituted PDAs having side groups of $R{=}(CH_2)_mOCONHC_2H_5$ with various lengths of inner alkyl chain ($m = 4$, 5, and 6)

2. Experimental

Urethane-substituted diacetylenes with various lengths of alkyl chain ($m = 4$, 5, and 6) (Fig. 1) were synthesized as described previously [17,18]. ω-Bromo alcohol ($Br(CH_2)_mOH$) with various lengths ($m = 4$, 5, and 6) was protected as *tert*-butyldimethyltrimethylsilyl ether, followed by a treatment with lithium acetylide–ethylene diamine complex to give the acetylene derivatives. After removing

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[*] Corresponding author. Tel.: +81-298-61-9273; fax: +81-298-61-2586.
E-mail address: h-tachibana@aist.go.jp (H. Tachibana).

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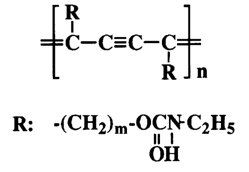

$$\mathrm{R:}\ -(\mathrm{CH_2})_m-\mathrm{O}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\underset{\underset{\mathrm{H}}{|}}{\mathrm{N}}-\mathrm{C_2H_5}$$

PDA-mUEt (m = 4, 5, 6)

Fig. 1. Chemical structures of urethane-substituted polydiacetylenes studied in this work.

the trimethylsilyl group under acid conditions, the resulting ω-hydroxy acetylenes were subject to a reaction with ethylisocyanate to give urethane-substituted acetylenes. The desired diacetylene monomers with various lengths were obtained by oxidative coupling reaction of the urethane-substituted acetylenes in the presence of copper(I)chloride and tetraethylenediamine.

Single crystals of the monomer were grown by slow evaporation of the ethylacetate solution. The monomer crystals were sealed in Pyrex tubes under vacuum and the polymerization was carried out by ^{60}Co γ-radiation with a dose of 60 Mrad. The corresponding ethylurethane-substituted polydiacetylenes are referred to as PDA–*m*UEt ($m = 4$, 5, and 6) We estimated the degree of polymerization from weight loss after dissolving respective γ-irradiated crystals in chloroform. The weight loss was less than 1%, indicating that the polymerization proceed almost completely for all the urethane-substituted diacetylene monomers investigated here.

3. Results and discussion

Fig. 2 shows reflectance spectra polarized parallel to the polymer backbone at 300 K for PDA–*m*UEt single crystals with $m = 4$, 5, and 6. For comparison, the reflectance spectra after phase transition at higher temperatures are also shown in Fig. 2. There are several common features in the reflectance spectra, irrespective of the length (m) of alkyl chains. One is that the reflectance spectra at room temperature (300 K) show the nearly identical structure, which corresponds to the A phase (blue phase). The strong peak polarized parallel to the polymer backbone is observed around 1.9 eV together with its vibronic sidebands, which has been assigned to the lowest ^1B_u exciton [13,19,20]. The other is that the lowest exciton peak shifts to higher energy and that the spectral feature becomes broader with increasing temperature, indicating that the A-to-B phase transition occurs. To be noted is, however, that the phase transition temperature depends on the alkyl chain length.

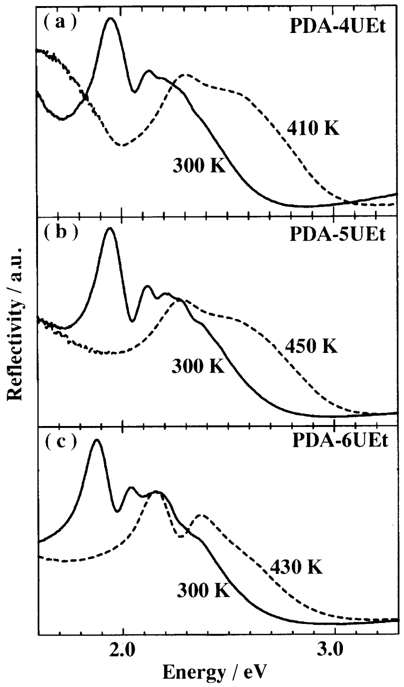

Fig. 2. Reflectance spectra at 300 K for a PDA–*m*UEt crystal: (a) $m = 4$, (b) $m = 5$, and (c) $m = 6$. Dashed lines represent the reflectance spectra for respective PDA–*m*UEt crystals above the phase transition temperature.

To clarify the chain-length dependence of the thermochromic phase transition, we investigated temperature dependence of reflectance spectra for PDA–*m*UEt crystal. The change of the reflectivity of the lowest exciton peak for respective PDA–*m*UEt is plotted as a function of temperature in heating and cooling runs in Fig. 3. The thermochromic behaviors clearly show an even–odd effect for the alkyl chain length, independence of the heating/cooling rate. As the temperature increases, the intensity of the exciton peak due to the A phase for all the PDA–*m*UEt crystals

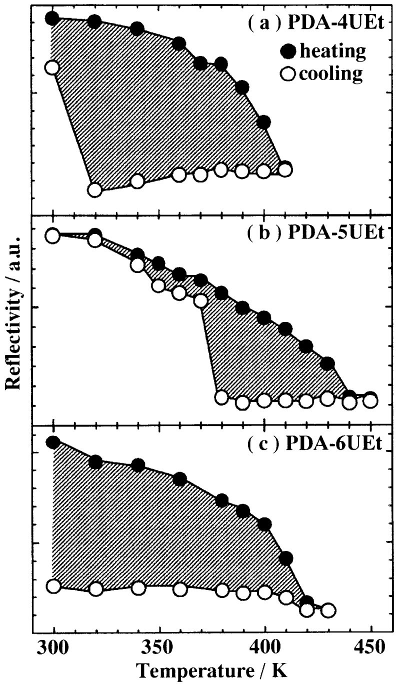

Fig. 3. Temperature dependence of the reflectivity peak (at 1.9 eV) of the lowest exciton in the low-temperature phase (A phase) for PDA–*m*UEt crystals: (a) $m = 4$, (b) $m = 5$, and (c) $m = 6$.

Table 1
Calorimetric data of PDA–*m*UEt ($m = 4$, 5, and 6) (see text)

	T_1 (K)	ΔH_1 (kcal/mol)	T_2 (K)	ΔH_2 (kcal/mol)	T_3 (K)	ΔH_3 (kcal/mol)
PDA–4UEt	394	1.14	482	3.97	333	0.60
PDA–5UEt	434	1.51	506	7.18	365	1.51
PDA–6UEt	415	1.56	464	5.67	401	0.80

decreases, corresponding to the A-to-B phase transition. In the cooling run, however, different behaviors were observed depending on the alkyl chain length. The odd-numbered PDA–5UEt crystal shows the reversible change from the B to A phase, accompanying an appreciable thermal hysteresis. On the other hand, the peak inherent to the B phase for the PDA–4UEt crystal does not revert completely to the initial state (A phase). Furthermore, the PDA–6UEt crystal remains in the B form even when cooled down to room temperature.

We also analyzed the thermochromic phase transition in PDA–*m*UEt crystals by differential scanning calorimetry (DSC). The phase transition temperature was determined as the maximum point on the endo- or exotherm, and the enthalpy change was evaluated from the integrated area of the peak profile. The results are summarized in Table 1. The DSC thermogram for all the PDA–*m*UEt crystals shows two endothermic peaks (T_1 and T_2) in the heating run. The first peak (T_1) corresponds to the A-to-B phase transition temperature, which is consistent with that determined by the spectroscopic change, as shown in Fig. 3. In addition, the phase transition temperature shows an even–odd effect for the alkyl chain length. The phase transition is likely to be governed by trans-to-gauche conformational changes of the alkyl chains (m), as investigated by ^{13}C NMR spectroscopy on the PDA–4UEt [21]. The second peak (T_2) shows a larger enthalpy change (ΔH_2), compared with that (ΔH_1) for the first one, which is caused by the scission of hydrogen bonding between urethane groups [10].

In the cooling run once after heating the crystals to a temperature between T_1 and T_2, the DSC thermogram shows an exothermic peak (T_3) for all the PDA–*m*UEt crystals but the corresponding enthalpy (ΔH_3) depends on the alkyl chain length. The results are also summarized in Table 1. In the case of PDA–5UEt crystals the enthalpy change ΔH_3 in the cooling run is nearly equal to the enthalpy change ΔH_1 in the heating run, while in the case of even-numbered PDA–*m*UEt crystals the corresponding two enthalpies are different. The difference in the DSC thermogram between even- and odd-numbered PDA–*m*UEt crystals reflects the spectroscopic feature whether the B phase after the phase transition can revert to the A one when cooled down to room temperature. In the cooling run, the PDA–4UEt crystal reverts to the initial A phase only partially, while the PDA–6UEt crystal remains in the B phase. Probably the difference in the inner alkyl chain length between the urethane groups and the polymer backbones affect the potential barrier of the free energy between the two (A and B) phases.

4. Conclusions

We have demonstrated that the thermochromic phase transition shows an even–odd effect for the inner alkyl chain length (m) of PDA–*m*UEt ($m = 4$, 5, and 6) the thermochromism due to the A–B phase transition is reversible and irreversible for PDA–5UEt and even-numbered ($m = 4$ and 6) PDA–*m*UEt, respectively. The even–odd effect for the thermochromic phase transition is reflected in the difference in two enthalpy changes corresponding to endo- and exothermic peaks in heating and cooling runs, respectively. The irreversible phase transition from the A to B phase by other stimuli such as photo-excitation will be realized at room temperature by utilizing the bistable electronic state for PDA–6UEt crystal.

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