Crystal Structures, Polymerization, and Thermochromic Phase Changes in Urethane-Substituted Diacetylenes Crystals with Varying Alkyl Chain Lengths

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A series of urethane-substituted diacetylene monomers (DA-*m*UPh) with different alkyl chain length (m = 4, 5, and 6) in side-chain substituents of $(CH_2)_mOCONHC_6H_5$ was synthesized. X-ray structural analyses for the DA-*m*UPh single crystals show that the monomers are packed by hydrogen bonding between the urethane groups, but the arrangement of the diacetylene moieties depends on the alkyl chain length. The reactivity of the DA-*m*UPh crystals upon γ-irradiation is different depending whether the alkyl chain length (m) is odd or even. The difference can be explained by the distance between the neighboring carbon atoms of the diacetylene groups. The temperature dependence of reflectance spectra for the polydiacetylene crystals has also been investigated. The thermochromic behavior is argued in comparison with the analysis of the differential scanning calorimetry.

Introduction

Diacetylenes are known to undergo solid-state polymerization on irradiation by UV light or γ-rays.[1−6] Two spectroscopically distinct forms, A (blue) and B (red) forms, have been observed for π-conjugated polydiacetylenes (PDA) in single crystals, Langmuir−Blodgett films, vacuum-deposited films, cast films, and bilayers dispersed in water. Much work has been done on the characterization and polymerization of various diacetylenes derivatives. Among them, poly(ETDU) [5,7-dodecadiyne-1,12-diol bis(ethylurethane)] is typical of the PDAs that exhibit a reversible thermochromic transition between the A and the B form.[7] The hydrogen bonding between the urethane groups plays an important role in the reversible thermochromic behaviors, which have been analyzed by various measurements such as X-ray diffraction, NMR, UV−visible, IR, and Raman spectroscopy.[8] Recently, photoinduced phase transitions between the two forms have been also reported in one of those urethane-substituted PDA, a single crystal of poly-4U3 [5,7-dodecadiyne-1,12-diol bis(propylurethane)].[9]

The alkylurethane-substituted PDAs have two kinds of alkyl chains in the side group; one is an inner alkyl chain between PDA backbones and urethane groups, and the other one is an outer alkyl chain outside the urethane groups. Little is known on the effect of inner alkyl chain length on the structure and thermochromic behavior of the urethane-substituted PDAs,[10,11] though the rather minimal effect of the outer alkyl chain length has been well investigated.[12]

In this paper, we report the synthesis of a series of urethane-substituted diacetylenes having side groups of R = $(CH_2)_mOCONHC_6H_5$ with various lengths of inner alkyl chain (m = 4, 5, 6). The effect of the alkyl chain length on topochemical polymerization was investigated in conjunction with the X-ray crystallographic analysis of the single crystals. Thermochromic behaviors of the derived PAD crystals were also studied by measurements of UV−visible reflectance spectra and differential scanning calorimetry.

Experimental Section

Urethane-substituted diacetylenes having side groups of R = $(CH_2)_mOCONHC_6H_5$ with various lengths of alkyl chain (m = 4, 5, 6) were synthesized as described previously (Chart 1).[13,14] ω-Bromo alcohol derivatives were protected as $^tBuMe_2$-Si (*tert*-butyldimethylsilyl) ethers, followed by treatment with lithium acetylide−ethylenediamine complex to give the acetylene derivatives. After deprotection of the $^tBuMe_2Si$ groups with methanesulfonic acid, the obtained acetylene alcohol was converted to the urethane-substituted acetylenes by reaction

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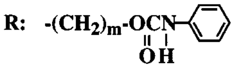
Chart 1. Chemical Structures of Diacetylene Monomers Used in This Study

R−C≡C−C≡C−R



$R: -(CH_2)_m-OC(=O)NH-C_6H_5$

DA-mUPh (m = 4, 5, 6)

Table 1. Crystal Data at 293 K for DA-*m*UPh (*m* = 4, 5, 6)

DA-*m*UPh	4	5	6
space group	$P2_{1/a}$	$P2_{1/a}$	$P2_{1/n}$
crystal system	monoclinic	monoclinic	monoclinic
a (Å)	11.95	12.96	5.21
b (Å)	5.11	5.14	39.76
c (Å)	19.1	19.36	7.01
β (deg)	92.64	95.53	108.7
V (Å^3)	1165.1	1283.0	1376.0
Z	2	2	2
d_{calcd} (g cm^{-3})	1.23	1.19	1.18
μ(Mo−Kα) (cm^{-1})	0.83	0.80	0.78
F(000)	432	464	496
no. of reflections	1357	1437	1132
no. of variables	144	153	162
R	0.064	0.060	0.076
R_w	0.066	0.078	0.074

with phenyl isocyanate. The desired urethane-substituted diacetylenes were obtained by oxidative coupling of the acetylenes.

Single crystals of the monomer were grown by slow evaporation of the ethyl acetate. 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 monomer and polymer of urethane-substituted diacetylenes with phenyl group used in this study are abbreviated as DA-*m*UPh and PDA-*m*UPh (*m* = 4, 5, 6), respectively.

The crystallographic data were collected at 20 °C on an imaging plate system (Rigaku RAXSI-IV) with Mo−Kα radiation. The structure was solved with the TEXSAN software package of the Molecular Structure Corp. and refined with Ortep-III. Other experimental details are summarized in Table 1.

Polarized reflectance spectra of the PDA-*m*UPh crystals were measured in the normal-incidence condition by using a premonochromatized halogen lamp. The crystals were held at a constant temperature controlled within ±1 K. Differential scanning calorimetry (DSC) measurements were performed on the polymer samples sealed under argon in silver puns. A heating/cooling rate of 5 K min^{-1} was used. Phase transition temperatures were determined as the maximum points on the endo- and exotherms, and the enthalpies were evaluated from the integrated area under the curves.

Results and Discussion

X-ray Analysis for Monomer Crystals before Polymerization. The effect of alkyl chain length on the crystal structure was investigated by X-ray diffraction measurements of single crystals of DA-*m*UPh. The crystallographic data are summarized in Table 1. Figure 1 shows the crystal structure of (a) DA-4UPh, (b) DA-5UPh, and (c) DA-6UPh. DA-4UPh and DA-5UPh crystallize in the monoclinic system. The space group is $P2_{1/a}$. The regular arrangement of diacetylene groups along the *b* axis is formed by hydrogen bonding between the urethane groups. DA-6UPh also crystallizes in the monoclinic form (β = 108.7°) but has a $P2_{1/n}$ space group. The difference in the cell parameters is merely due to the choice of the setting. The diacetylene groups stack along the *a* axis, but the packing manner between the stacks is different from that of DA-4UPh and DA-5UPh, as shown in Figure 2.

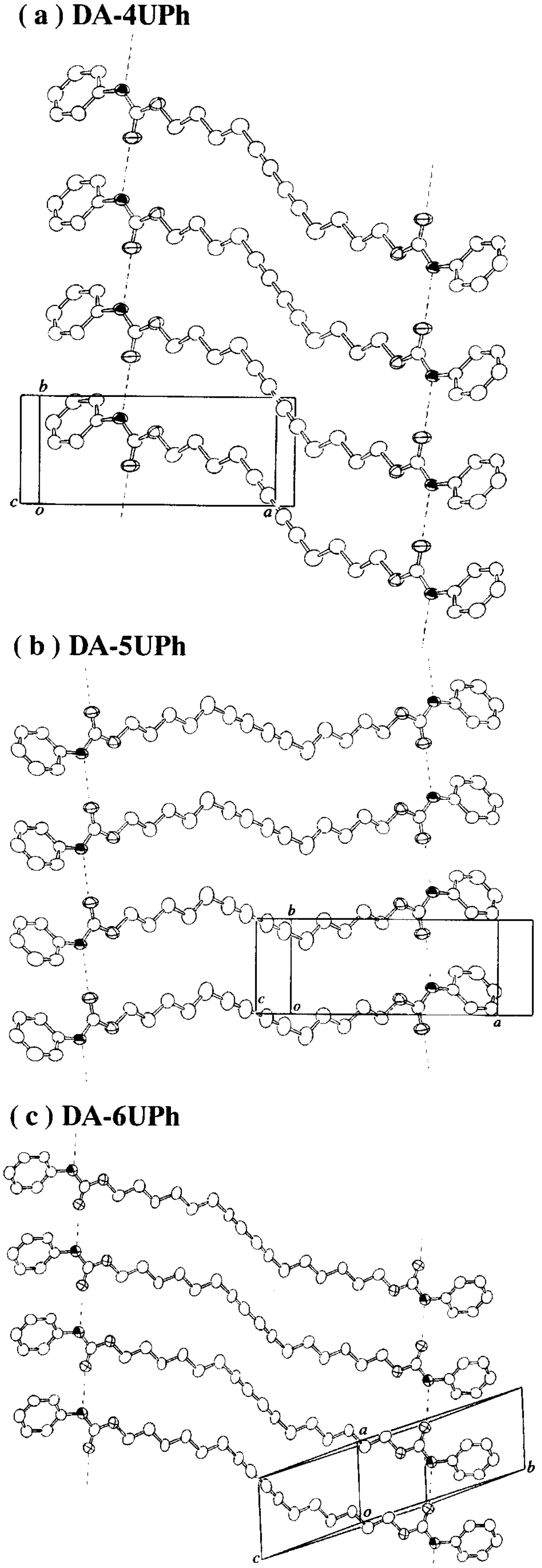
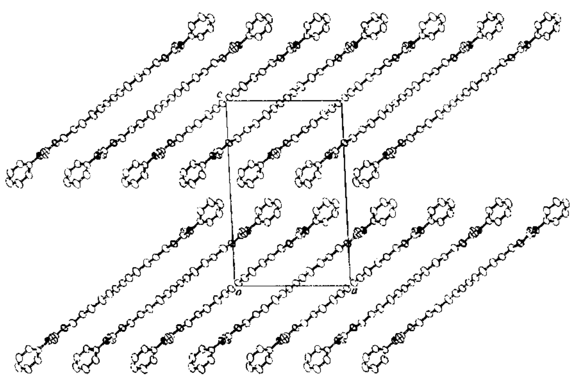


Figure 1. Crystal structure of (a) DA-4UPh, (b) DA-5UPh, and (c) DA-6UPh.

From the analysis of the obtained data, we estimated the intermolecular distance *R* between reacting carbons,

(a) DA-4UPh



(b) DA-6UPh

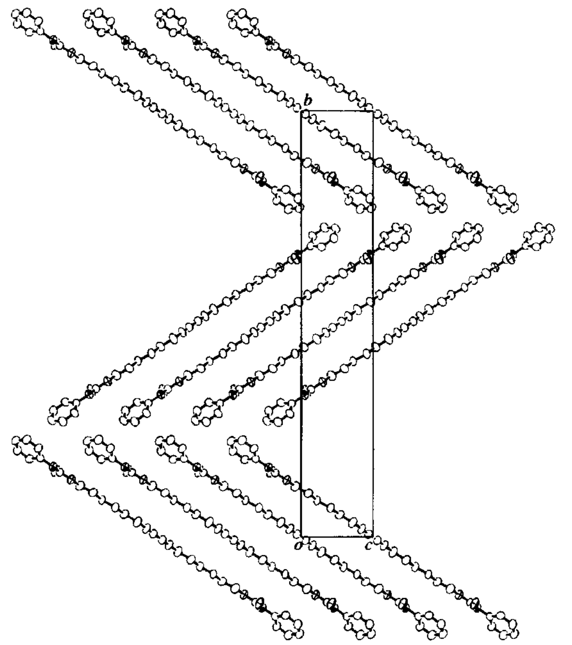


Figure 2. Crystal structure of (a) DA-4UPh and (b) DA-6UPh viewed along the *b* and *a* axes, respectively.

Table 2. Distance between Reacting Carbons (*R*), Stacking Distance (*d*), and Angle between the Diacetylene Rod and the Stacking Axis (ϕ) for DA-*m*UPh (m = 4, 5, 6)

DA-*m*UPh	4	5	6
R (Å)	3.53	5.20	3.57
d (Å)	5.11	5.14	5.21
ϕ (deg)	43.7	69.3	43.3

the stacking distance *d* between neighboring diacetylene moieties along the stacking axis, and the inclination angle ϕ between the diacetylene rod and the stacking axis. The solid-state polymerization of diacetylenes in crystal is known to critically depend on the above three parameters.[15,16] The ideal criteria (*R*, *d*, and ϕ) for the polymerization is <4 Å, 5 Å, and 45°, respectively. These parameters for three DA-*m*UPh crystals are summarized in Table 2. The three parameters depend on the alkyl chain length. The stacking distance (*d*) was nearly identical (5.1−5.2 Å) for all the DA-*m*UPh crystals, because the arrangement of the diacetylene moieties is determined by the hydrogen bonding between the urethane groups.

The other two parameters for DA-5UPh crystals were found to be quite different from those of DA-4UPh and -6UPh crystals. In general, it is well-known for molecular crystals of *n*-alkanes that physical properties such as crystal structure and melting point depend on whether the number of methylene units is odd or even.[17−20] Such an even−odd effect of the alkyl chain length was also observed clearly in packing structures of the diacetylene moieties. In the case of the even-*m* chain length, the diacetylene moieties take a packing structure suitable for solid-state polymerization, while DA-5UPh crystals are outside the suitable range for polymerization reactivity. The direction of the hydrogen bonding between the urethane groups for the DA-5UPh crystals is opposite, compared with those for the DA-*m*UPh crystals with even-*m* chain, which arises from the difference of one methylene length. The increase in ϕ of the DA-5UPh crystals is due to the difference in the direction of the hydrogen bonding, resulting in the increase in *R*.

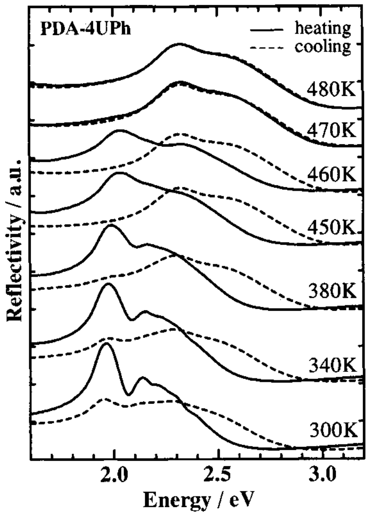


Figure 3. Temperature dependence of reflectance spectra for a PDA-4UPh crystal. Solid and broken lines represent the spectra in heating and cooling runs, respectively.

To clarify the degree of polymerization on irradiation of γ-ray, we measured weight loss after dissolving respective γ-irradiated crystals in chloroform. The estimated conversions to the polymer for DA-*m*UPh (m = 4, 5, and 6) are 95%, 0%, and 70%, respectively, indicating that the DA-5UPh crystals do not polymerize upon γ-irradiation. This result is consistent with the diacetylene packing structures hitherto known[15,16] and described above. From now on, we focus on the PDA-4UPh and PDA-6UPh crystals after polymerization.

Thermochromic Behavior of PDA-*m*UPh (m = 4, 6) Crystals. We measured temperature dependence of reflectance spectra (polarized parallel to the polymer backbone) of single crystals of PDA-4UPh. As shown in Figure 3, after polymerization with irradiation of γ-ray, the ^1B_u exciton peak assigned to the A form[12,21,22] is

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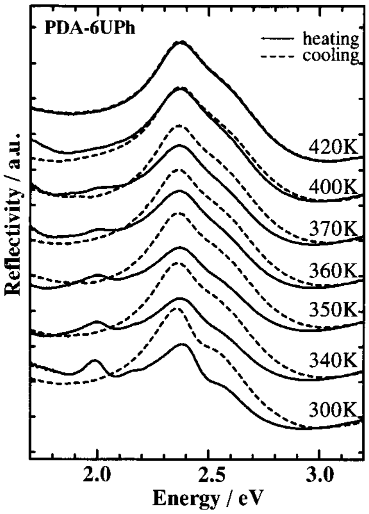

Figure 4. Temperature dependence of reflectance spectra for a PDA-6UPh crystal. Solid and broken lines represent the spectra in heating and cooling runs, respectively.

observed at 1.96 eV. The peak at its higher energy corresponds to vibronic side bands associated with the double-bond stretching of the conjugated backbone. Upon heating, the crystals undergo the phase transition into the B form and the peak energy shifts to 2.3 eV, in agreement with the behavior reported in the literature.[23] The critical temperature for the A-to-B transition is in the range of 460−470 K. The B form did not completely revert to the initial A form even when cooled to room temperature (300 K).

Figure 4 shows temperature dependence of reflectance spectra (polarized parallel to the polymer backbone) for the PDA-6UPh crystals. An intense peak due to the lowest exciton of the B form is observed around 2.4 eV, in addition to the weak exciton peak due to the A form around 2 eV. This indicates that the two forms are both contained in the PDA-6UPh crystal as polymerized at room temperature. Upon heating, the weak exciton peak due to the A form around 2 eV decreases and finally disappears, indicating that the A form totally changes into the B one. Upon cooling to room temperature, the PDA-6UPh crystals remained in the B form with no revival of the A form.

To quantify the thermochromic phase transition, we performed differential scanning calorimetry (DSC) on PDA-4UPh and PDA-6UPh crystals. Two endothermic peaks were observed in the DSC thermogram in the heating process. The first endothermic DSC peak, at T_1, which corresponds to the A-to-B transition of the polymer backbones, is likely to be governed by a concomitant trans-to-gauche transition of alkyl chain between the urethane group and the polymer backbones.[24] The second peak (T_2) is due to the scission of the hydrogen bonds between the urethane groups attached to the PDA backbones.[12] The results are summarized in Table 3. The estimated enthalpy change ΔH increases with the increase in the alkyl chain length, as also shown in Table 3. T_1 in the DSC for the PDA-4UPh and the PDA-6UPh crystal seems to be well consistent with the respective A-to-B transition temperatures in the reflectance spectra, although the peak characteristic of the A form is too small in the reflectance spectra for the PDA-6UPh crystals to accurately determine the A-to-B phase transition temperature from the spectral change.

Table 3. Calorimetric Data of PDA-*m*UPh (m = 4, 6)[a]

	T_1 (K)	T_2 (K)	T_3 (K)	ΔH_1 (kcal/mol)	ΔH_2 (kcal/mol)	ΔH_3 (kcal/mol)
PDA-4UPh	460	510	364	2.08	1.94	0.65
PDA-6UPh	424	475	379	3.61	4.01	0.64

[a] See text.

Analyzing the DSC results in detail, a small and broad exothermal peak (T_3) corresponding to the B-to-A transition was discerned in the cooling runs, after the crystal was once heated to a temperature between T_1 and T_2, for both PDA-4UPh and -6UPh crystals. As shown in Table 3, the estimated enthalpy change (ΔH_3) at T_3 is appreciably smaller than those at T_1. The irreversible thermochromic behavior of the B-to-A transition can be explained by the difference in the enthalpy change, which may arise from the apparent decoupling between the structural transitions occurring on the inner alkyl chain and on the polymer backbone (responsible for the thermochromism). However, these crystals were observed to go back to the A form slowly over several days while kept at room temperature.

Conclusion

We synthesized urethane-substituted diacetylenes (DA-*m*UPh) with different alkyl chain length (m = 4, 5, and 6). The packing structure of diacetylene moieties was investigated by X-ray crystal structure analysis of the corresponding monomers. The DA-4UPh and DA-6UPh crystals polymerized upon γ-irradiation, while no polymerization occurs in the DA-5UPh crystal. The even−odd effect of the methylene number of the alkyl chain is clearly reflected in the two parameters, the angle between the diacetylene rod and the stacking axis and the distance between the neighboring reacting carbon atoms, which both govern the polymerization reactivity. We investigated thermochromic behaviors by measuring the temperature dependence of reflectance spectra for the PDA-4UPh and PDA-6UPh crystals after polymerization. Upon heating, A-to-B phase transition was observed in the reflectance spectra. The B form does not revert to the initial state instantaneously even when cooled to room temperature. The incomplete reversibility of the thermochromic transition is reflected in the difference in the enthalpy changes for the A-to-B and B-to-A transition.

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Supporting Information Available: A figure detailing the atomic numbering scheme for DA-*m*UPh molecules and tables of crystal data, bond lengths and angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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