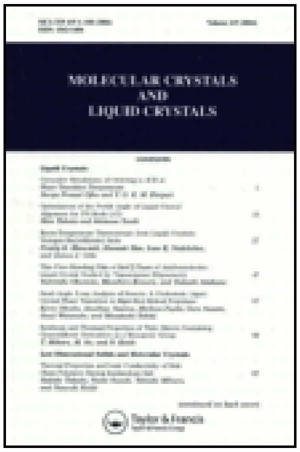

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Photo- and Thermo-Chromic Behaviors of Polydiacetylenes with Alkylurethane Substituents

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PHOTO- AND THERMO-CHROMIC BEHAVIORS OF POLY-DIACETYLENES WITH ALKYLURETHANE SUBSTITUENTS

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Abstract A series of polydiacetylenes with alkylurethane substituents R = $(CH_2)_4OCONHC_nH_{2n+1}$, where n= 1-18, have been synthesized and their chromic behaviors have been studied by optical spectra, X-ray and DSC measurements. All of these polydiacetylenes exhibit the reversible thermochromic transitions, unless the samples are heated exceeding the limited temperatures, while the photo-excitation results in irreversible color change, only from blue to red.
The length of the terminal alkyl unit in the side groups are found to affect the thermal hystereses from 0 to 60K in width.

INTRODUCTION

One of the specific characteristics of polydiacetylenes is the chromic behaviors, which is demonstrated by the drastic color change, usually between blue and red. The differece of colors is explained by the corresponding effective conjugation length on polymer backbones, being induced by disorder or distortion of side groups.

The popular examples are given by poly(nBCMU) with side groups R = $(CH_2)_nOCONHCH_2COOC_4H_9$, whose chromic transitions are closely related to the formation and the disruption of the inter-urethane hydrogen bonded networks.1) On the contrary, in the case of poly-ETCD with more rigid side groups R = $(CH_2)_4OCONHC_2H_5$, phase transition takes place reversibly in the limited temperature region without the disruption of hydrogen bondings.2) With the interests of side group dependency of chromic behaviors, we have synthesized polydiacetylenes with substituents R = $(CH_2)_4OCONHC_nH_{2n+1}$ (abbreviated as poly-C_4UC_n) by changing the terminal (outer) alkyl-chain length.

RESULTS AND DISCUSSION

Poly-C_4UC_n with metallic brilliance are spectroscopically blue (blue-phase:A-phase) with reflectance maxima at about 1.9 eV at 290K due to the ^1B_u exciton transition strongly polarised along the polymer chain axis. On heating up to 420 K or by UV-light irradiation, polymers turn red with peaks at about 2.3 eV (red-phase:B-phase). Fig.1 shows the correspondence of the reflectance intensity at 1.94 eV (A-phase peak) and DSC thermogram. The crytical temperatures for the A-to-B transition in the heating process (T_2) and for the B-to-A transition (T_1) have been determined taking half points of the reflectivity change or by DSC data. The reflectivity trace shown in Fig.1(a) draws a typical hysteresis loop due to the reversible A-B transition. When temperature is increased beyond polymer melting temperature (T_3), the reflectivity at 1.49 eV does not recover in the cooling run and A-B transition becomes irreversible. T'_3 is the temperature of solidification of once molten polymer heated exceeding T_3. When the sample is heated up to 500K, no distinct hysteresis loop can be seen as is given in Fig.1(b).

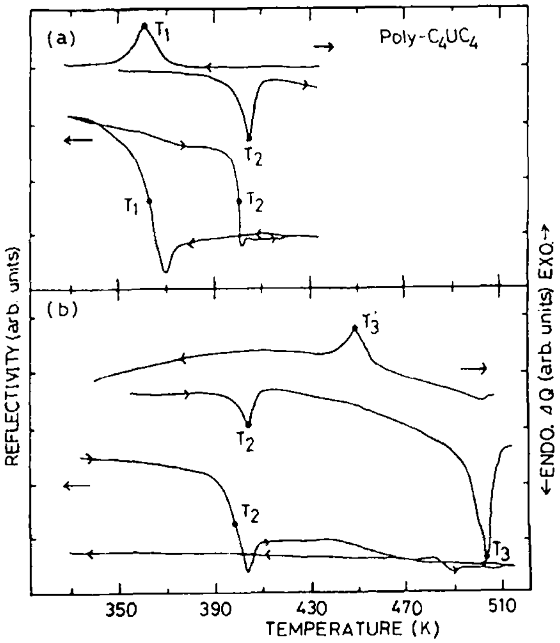

Fig.1 DSC thermogram and relfectivity at 1.94 eV

The phase diagram indicating T_1, T_2 and T_3 dependency on the terminal alkyl-chain length is given in Fig.2.
The change in enthalpy upon the A-B transition can be approximately estimated from the integrated area of the DSC endothermic peak at T_2. The enthalpy change appears to increase linearly with $n \leq 5$, but tend to decrease with $n > 6$. The initial increase in enthalpy with n indicates additive contribution of the conformational change in the terminal alkyl -groups to the total free energy. However, polymers with longer alkyl-chains, thermodynamics of the A-B transition is increasingly affected by the order-disorder type conformational change in the terminal alkyl-chains.

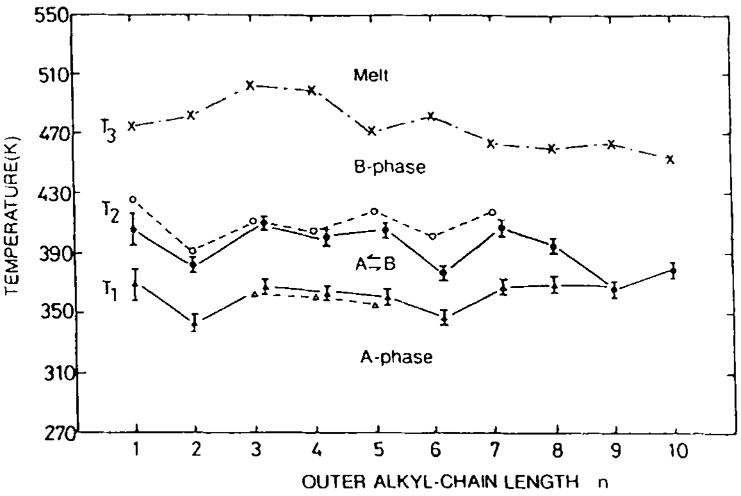

Fig.2 Phase diagram of poly-C_4UC_n

In Fig.3 is shown the thermal changes in optical spectra of poly-C_4UC_5 crystals. The reflectance spectra of the exciton (a) and Raman Spectra of the -C=C- stretching mode in the polymer backbone (b) at 299 and 418K are clearly indicating the difference of A- and B-phase, while the IR absorption spectra of the N-H stretching modes show little change at two temperatures. The results indicate that the degree of hydrogen bonding is essentially unchanged during the A-B phase transition. At the bottom of Fig.3 are shown the respective spectra measured at room temperature on the sample once heated up to 510K , exceeding T_3. B'-phase sample shows a rather similar spectra (reflectance and Raman) to that in the B-phase, but with less intensity and blurred profile.

Temperature-variation of the IR band intensity or the degree of hydrogen bonding is protted in Fig.4 for two types of thermal cycles : (A) $T_2 < T < T_3$ and (B) $T > T_3$. In the first run, T_1or T_2 are fully recovered in cooling run but in the case of (b), the hydrogen bonds are collapsed around T_3 and only about a half of the absorbance is recovered around T'_3. Thus the role of hydrogen bonding in the reversible therochromic system is clearly demonstrated.

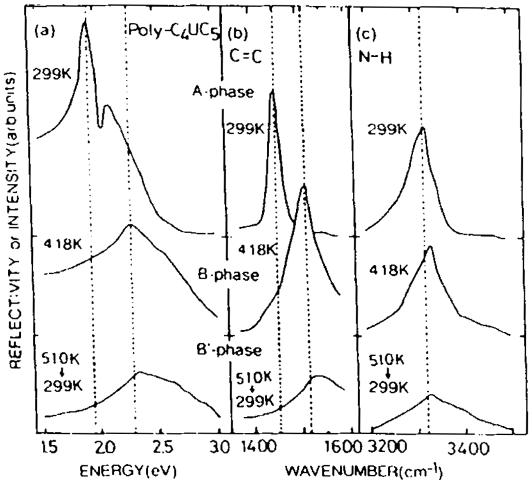

Fig.3 Optical spectra of A, B and B'-phase

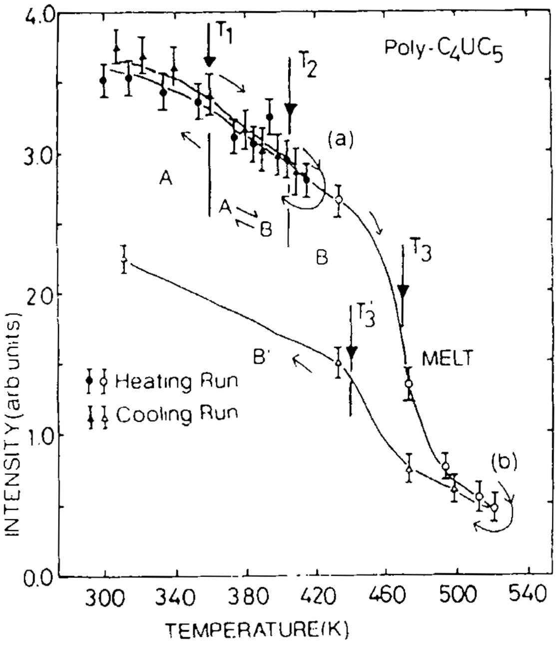

Fig.4 Temperature-variation of IR band intensity (N-H stretching)

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