Reversible Color Changes of Polydiacetylene Induced by Monomer Solid Phase Transition

Kotaro Araya
Advanced Research Laboratory, Hitachi Ltd., Hatoyama, Saitama 350-03

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Synopsis. Color change associated with solid phase transition is observed in the diacetylene derivatives, partially polymerized 4,6-decadiyne-1,10-bis(propylurethane). Moreover, the temperature of this color change can be altered by mixing with other derivatives.

Polydiacetylene,-(-RC=C=C=CR-$)_n$-, belongs to a unique class of polymers obtained by topochemical polymerization of a diacetylene(1,4-disubstituted 1,3-butadiyne) monomer in the solid state upon either thermal annealing or exposure to high energy radiation.(1) The polymers are colored either red, purple, or blue because π-electrons are delocalized along the conjugated backbone. The polymers also exhibit several types of color change; namely, thermochromism,(2,3) solvatochromism,(4–6) and photochromism.(7,8)

This paper reports a color change triggered by a solid phase transition of a diacetylene monomer. Color changes of polydiacetylene are understood to be due to changes in the length of the conjugated chain and/or in the planality of the polymer backbone. Therefore, the change would be caused by differences in the packing condition of the conjugated backbone. In the partially polymerized diacetylene, the polymer chain is dissolved in a monomer matrix and it forms a solid solution with a monomer. If a diacetylene monomer has a solid phase transition, changes in the packing condition of the polymer chains would be induced, leading to a color change. This type of color change has been reported only for the partially polymerized 1,6-di(1-carbazolyl)-2,4-hexadiyne.(9) The transition temperature, however, is very low (142 K) and, of course, unchangeable. This low temperature constrains other measurements and applications.

With this in mind, diacetylenes have been extensively synthesized in search of a diacetylene with a solid phase transition at a proper temperature, which would make this transition temperature changeable. Suitable diacetylenes are reported here. These compounds are 4,6-decadiyne-1,10-bis(propylurethane), R=-$(CH_2)_3$-$CONHC_3H_7$ and 4,6-decadiyne-1,10-bis-(butylurethane), R=-$(CH_2)_3$-$CONHC_4H_9$. Hereafter, these compounds are designated as 3PU and 3BU, respectively. These compounds were prepared according to a procedure reported by Patel.(10) The calorimetric data were recorded with a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC). The respective melting points of 3PU and 3BU were 117.6 °C and 110.0 °C. The solid phase transition of 3PU was observed at 76.6 °C and it was reversible.

A crystalline 3PU monomer is a white powder and turns blue upon exposure to daylight. The polymer content of this partially polymerized sample is about 1 wt%. The polymer conversion was determined by extracting a monomer with acetone using a Soxhlet extractor and weighing the residual polymer. Solid state absorption spectra were measured using a Hitachi U-3400 spectrophotometer with reflectmetric

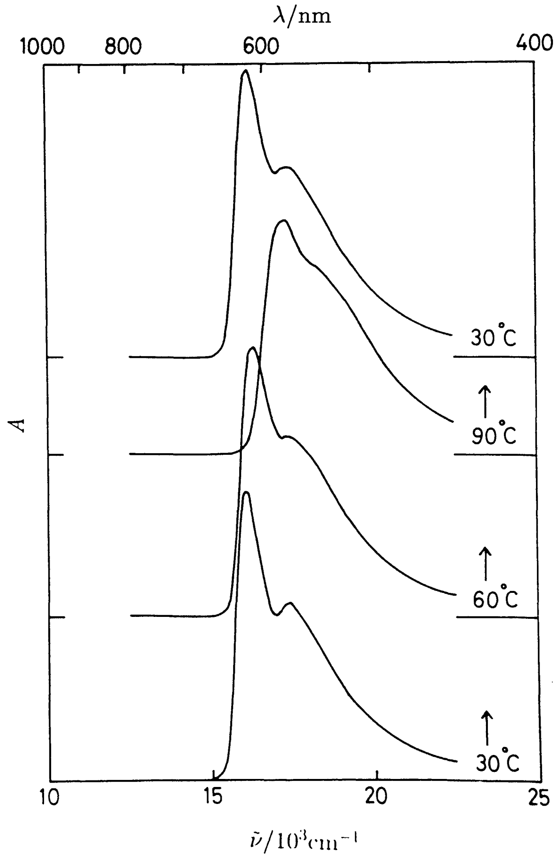

Fig. 1. Absorption spectra of partially polymerized 3PU.

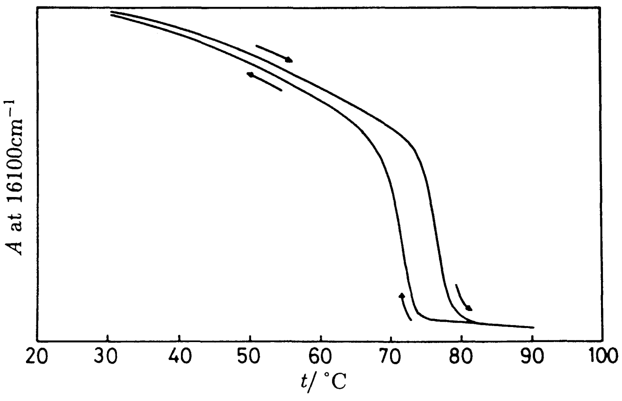

Fig. 2. Temperature dependence of absorbance at 16100 cm^{-1} of partially polymerized 3PU.

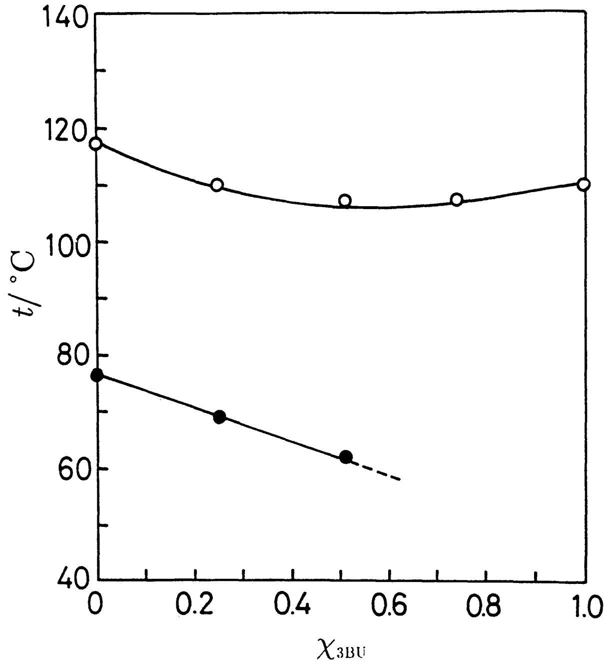

Fig. 3. Phase diagram of the 3PU-3BU system. Open circles: melting points. Closed circles: solid phase transition temperatures.

equipment, and were derived from diffuse reflection spectra of the solid dispersed in powdered sodium chloride. The temperature dependences of the absorption spectra are shown in Fig. 1. The maximum at 30 °C is located at 16100 cm^{-1} (620 nm). The spectrum at 60 °C is almost the same as at 30 °C. A large blue shift, however, is observed at 90 °C, when the color changed to purple. The maximum is shifted to 17200 cm^{-1} (580 nm). The spectral shift amounts to about 1100 cm^{-1}. When the solid is cooled to 30 °C again, the maximum turns back to 16100 cm^{-1}. For a detailed study of the temperature dependences of these spectra, the absorbance at 16100 cm^{-1} was monitored as a function of temperature. The results are shown in Fig. 2. During heating, absorbance drastically decreases at 76 °C and falls to almost zero at 80 °C. During cooling, absorbance sharply increases at 75 °C. This spectral change is reversible, and the temperature coincides with the solid phase transition temperature of 3PU, 76.6 °C. It is therefore concluded that the spectral change is induced by the monomer phase transition.

The most interesting feature of this diacetylene derivative is that the temperature of this color change can be changed. The 3PU and 3BU compounds form a solid solution over the entire composition. The phase diagram of the 3PU-3BU system determined by DSC is shown in Fig. 3. The phase transition of 3PU observed at 76.6 °C is also clearly observed up to 50 mol% of 3BU. The transition temperature is reduced to 62.0 °C at 50 mol% of 3BU. Accordingly, the temperature of the color change can be varied from 76.6 °C to 62.0 °C. If many diacetylenes having a phase transition were found, the color change of this type would be attained at a desired temperature and could be more effectively applied, for example, as a thermoindicator.

Although many types of color change have already been reported, a detailed understanding of this phenomenon has not been attained. The system reported here may help in understanding the relationship between the electronic state and the structure of polydiacetylenes.

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