Preparation of Chiral Polydiacetylene Film from Achiral Monomers Using Circularly Polarized Light

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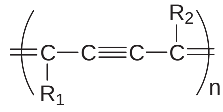
Formation of chiral polydiacetylene (PDA) film using circularly polarized light (CPL) was demonstrated for the first time. Commercially available achiral derivative of diacetylene was used to prepare the vacuum evaporated monomer film and it was polymerized using ultra-violet CPL. Chiral source was only CPL, and the irradiation of left- and right-CPL definitely yielded opposite chiral polymer.

PDA is one of the promising materials for the practical applications of optical, electrical, and biological devices. Large carrier mobility evaluated by the time-of-flight measurements[1] motivates us to employ these materials as electrical applications. Moreover, since PDA is well known as a quasi one-dimensional (1D) π-conjugated polymer, the specific carrier transport is expected due to the 1D electronic states. Thus, until now, these interesting electronic behaviors attract us to the intensive researches. In any case, structural control of the PDA backbone must be an essential process to bring out the useful function from PDA effectively. In chiral system, symmetric mirror plane disappears, and interaction between magnetic field and chiral materials plays an important role due to the pseudovector nature of magnetic field. Thus, introduction of chirality into the conjugated materials such as polydiacetylene is expectative to fruition of novel organic devices with special electro-magnetic functions.

The presence of chiral side-groups attached to the backbone or chiral dopant in the reaction field is generally required to introduce chirality into a polymer. Chiral structure of various π-conjugated polymers such as polythiophene,[2] polypyrrole,[3] and polyaniline[4] has been also reported. In these cases, introduction of chiral side-groups is general way to introduce macroscopic chirality. Akagi et al. reported the successful synthesis of the helical polyacetylene with a chiral nematic reaction field.[5] Interestingly, using the chiral dopant with opposite chirality can reverse the handedness of the helix. On the other hand, photoinduced chirality in achiral polymer liquid crystals containing azobenzene chromophores was demonstrated to realize the reversible switching between opposite chirality.[6] Photosensitivity and stiff nature of azobenzene liquid crystalline mesogen attached to the side-chain plays an important role in photoinduced chirality. There is no chiral side-group or dopant, and the only source of chirality is a circularly polarized light (CPL). Alternating irradiation of left- and right-CPL actually realizes the reversible switching between left- and right-handed helical structures. For the azobenzene case, any chemical reactions do not take place to form helical structure, but only structural change of side-group causes the macroscopic chirality. In this sense, enantioselective chemical reaction in the polymerization process without chiral side groups and chiral dopant is challenging target and actually interesting. In this letter, we demonstrate the formation of chiral PDA from the commercially available achiral derivative of diacetylene monomer using CPL for photopolymerization. Chiral source is only CPL, and the irradiation of left- and right-CPL can definitely yield opposite chiral polymers. This is the first time to report the CPL induced chiral formation in PDA. There was a report of the production of a highly enantioenriched compound higher than 99% ee by CPL, in conjunction with asymmetric autocatalysis.[7] To our best knowledge, however, there is no report available about the induced chirality into polymer during photopolymerized process.

Materials used is diacetylene derivative, TDA (10,12-tricosadiynoic acid, $CH_3(CH_2)_9C{\equiv}C{-}C{\equiv}C(CH_2)_8COOH$). TDA was purchased from Tokyo Chemical Industry Co., Ltd., and was used as received. The samples used in the circular dichroism (CD) and other optical measurements were the PDA films, which were polymerized from TDA monomer films deposited on fused silica substrate. The process pressure during deposition of TDA monomer was kept less than 2×10^{-4} Pa. Thickness of the TDA layer was approximately 60 nm. Poly(TDA) **1** (Chart 1) was obtained with a circularly polarized UV light generated using Babinet–Soleil prism from ultra-high pressure mercury lamp for 20 min. To avoid the variation between individual deposition batches, monomer films for left- and right-CPL irradiation were prepared at the same time. Intensity of the light was approximately 19.4 mW/cm^2. CD spectrum was measured using JASCO CD spectrometer J-715.

1:



$$\left(=\underset{R_1}{C}-C\equiv C-\overset{R_2}{C}= \right)_n$$

$R_1=(CH_2)_9CH_3$
$R_2=(CH_2)_8COOH$

Chart 1.

Figures 1a and 1b show the absorption and CD spectrum for poly(TDA) film. Solid and dashed lines represent the spectrum for the PDA film polymerized with left- and right-CPL, respectively. Absorption peak appeared at around 600 nm gradually increased with the polymerization time, and then saturated. As shown in the Figure 1, similar absorption spectrum was obtained for the PDA polymerized with different polarization condition, i.e., left- and right-CPL. As shown in Figure 1b, significant CD signals are observed at a wavelength from 500 to 700 nm where the absorption peak locates. Surprisingly, CD spectra for the PDA polymerized with left- and right-CPL clearly show the opposite sign. Namely, left- and right-circularly polarized UV light distinguishably produce the PDA film with opposite chirality as shown in Figure 1b. Although apparent CD signal can be observed from the film with birefringence due to in-plane orientation, significant CD signal was not observed from our PDA sample polymerized with linear polarized light. Moreover,

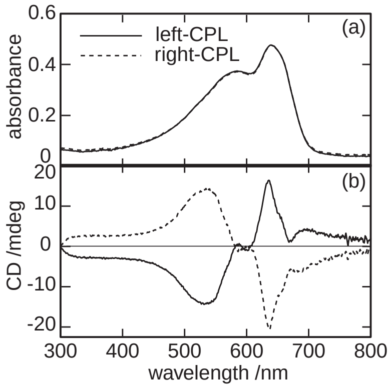


Figure 1. (a) Absorption and (b) CD spectrum for poly(TDA) film. Solid and dashed lines represent the spectrum for the film polymerized with left- and right-CPL, respectively.

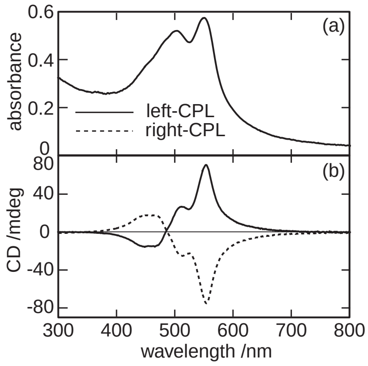


Figure 2. (a) Absorption and (b) CD spectrum for poly(TDA) film after annealing.

all films polymerized with CPL show the same sign of the CD signals.

It is well known that thermochromic phase transition takes place in PDA film at elevated temperature. PDA film changes its color from blue to red due to the shift of absorption peak. The blue-shift of the absorption peak is reasonably considered as the reduction of effective conjugation lengths due to the introduction of structural distortion into the polymer backbone. As shown in Figure 2a, absorption peak shifted from 650 to 550 nm due to the thermal treatment of the blue-form PDA films at a temperature of 80 °C for 10 min. Interestingly, optical chirality maintained during the phase transition, and the peak of the CD spectrum shifted according to the absorption peak (see Figure 2b). Detailed mechanisms of the thermochromic phase transition are still not understood. Theoretical calculations indicated that a rotation of only a few degrees about the single bond in PDA backbone dramatically changes the π-orbital overlap,[8] causing a blue-shift of the absorption spectrum. For the poly(TDA), rearrangement of the long alkyl side-groups that packed due to van der Waals interaction induces the small distortion of PDA backbone. This implies that only a small distortion could maintain the chiral structure of PDA. At the present stage, we have not obtained the direct picture of helical structure, which is presumably necessary for drawing out the electro-magnetic functions. However, presence of the optical chirality is precursor for the helical structure. In other words, optical chirality is certainly requirement for the helical structure. Now we are optimizing the condition for sample preparation. TEM or AFM image of the helical structure will be published elsewhere.

Successful preparation of chiral structure in PDA Langmuir–Blodgett (LB) film was also reported by Liu et al.[9] Under the specific conditions, chiral PDA LB films were spontaneously formed from achiral monomers. Particularly, both left- and right-handed chirality could be accidentally obtained in PDA film polymerized on a water surface, and sign of the chirality could not be controlled. They concluded that presence of the interface and metal ions in subphase is fundamental to the chiral formation. Unlike the PDA-LB films, no specific metal-ions is requisite and the chirality can be completely controlled using opposite CPL in the vacuum deposited PDA. At this stage, detailed mechanism of the chiral induction in the PDA backbone by the CPL polymerization is explored. Presumably, simultaneous photoexcitation of two-diacetylene monomers is definitely important to form PDA at the initial stage of the polymerization. Thus, interaction between the CPL and the diacetylene dimer possibly plays a key role in the enantioselective polymerization in PDA. The similar experiments using different monomers with various side-groups are now proceeding to reveal the mechanism of enantioselective polymerization. In our recent results, PDA using diacetylene monomer with long alkyl-chain compared with TDA as a side-groups, 10,12-pentacosadiynoic acid ($CH_3(CH_2)_{11}C{\equiv}C\text{–}C{\equiv}C(CH_2)_8COOH$), also shows chirality. To explore the relationship between molecular structure of side-groups and chirality is also helpful to increase the efficiency of the enantioselective polymerization.

In conclusion, formation of the chiral PDA from the commercially available achiral derivative of diacetylene monomer using CPL for photopolymerization was demonstrated. In this case, chiral source is only CPL, and the irradiation of left- and right-CPL can definitely yield opposite chiral polymers. Induced chirality was shown to be maintained after the thermochromic phase transition took place.

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