Synthesis of Polymers from Chiral Monomers in Chiral Liquid Crystals

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ABSTRACT: Polymer prepared from a monomer ((S)-configuration at stereogenic center) in a cholesteric liquid crystal (CLC) medium consisting of chiral molecules in (R)-configuration, a three-dimensional (3D) chiral continuum, exhibits intense Cotton effect compared to polymer prepared in the CLC with (S)-configuration. This result can be explained by intermolecular interaction between the monomer and the CLC medium in the polymerization process. The intramolecular twisted structure along the polymer chain (secondary structure) and the helical aggregation between the polymer chains (intermolecular structure and tertiary structure) induced by the liquid crystal medium as 3D chiral continuum are discussed. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 3586–3591, 2013

INTRODUCTION

Liquid crystal (LC) is an intermediate state between liquid and crystal, which has both liquid-like fluidity and crystalline-like orders. Low-molecular-weight LCs have been used in display devices because of their optical anisotropy and quick response to an external electric field, whereas LC polymers have been applied to engineering plastics because of their good processability and mechanical strength. These applications are based on characteristic properties of LCs such as good orientational property and flexibility in the LC phase.[1–7]

We previously conducted polycondensation of achiral monomers in enantiomeric cholesteric liquid crystals (CLCs)[8–11] instead of the generally used isotropic solvents such as tetrahydrofuran and toluene. CLCs possess a helically oriented director and a liquid-like fluidity. The polymers prepared in CLCs exhibited chiroptical activity due to a chiral stacking between polymer chains produced by the helically structured medium of the CLCs during the polymerization reaction, despite no central chirality in the monomer units.

Those results led us to consider polymerization of chiral monomers in CLCs and the structural chirality and chiroptical properties of the resultant polymers. In this study, we report the Migita-Kosugi-Stille polycondensation for a thiophene derivative bearing a chiroptically active side chain in CLCs. Chiroptical properties of the polymers thus obtained were examined with circular dichroism (CD) spectroscopy, and the chirality of the individual main chain and the structural chirality induced by the CLC medium are discussed.

EXPERIMENTAL

Materials and Methods

5,5′-Bis(trimethylstannyl)-2,2′-bithiophene was synthesized by the previously reported method.[8] ^{1}H-NMR spectra were taken with Jeol JNM-ECS 400. $CDCl_3$ was used for the NMR solvent. Chemical shifts are represented in parts per million downfield from tetramethylsilane (TMS) as an internal standard. Infrared (IR) absorption spectra were recorded with Jasco FT/IR-300 spectrometer. Ultraviolet–visible (UV–vis) absorption spectra of the polymers in chloroform were recorded with a JascoV-630 UV–vis optical absorption spectrometer. CD spectra were obtained with a Jasco J-720 spectrometer. Optical textures of the LCs were taken with a Nikon ECLIPSE LV100 polarizing optical microscope (POM) equipped with Linkam TH-600PM thermocontrol stage. The samples were sandwiched between two thin glass slides for the POM observations. Differential scanning calorimetry (DSC) analysis was conducted with Seiko Instruments DSC6200. A matrix assisted laser desorption/ionization time of flight mass (MALDI-TOFF MASS) spectrum of the monomer was recorded with AB Sciex TOF/TOF[TM] 5800. The specific optical rotation of the monomer was measured with Jasco Digital Polarimeter DIP-370.

Synthesis of Cholesteric Liquid Crystal Medium

CLC ((R)-LC and (S)-LC) used as reaction media in this study were synthesized according to the previously reported procedure.[8] Scheme 1 shows the chemical structure of the (R)-LC and (S)-LC. The (R)-LC has an anticlockwise helical molecular architecture, whereas the (S)-LC has a clockwise architecture in the CLC phase.[9] The standard components for CLC allow the formation of a mesophase in the mesophase temperature range.

Additional Supporting Information may be found in the online version of this article.
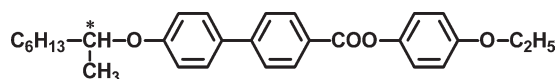
Scheme 1. Chemical structures of (R)-LC, (S)-LC. *, Stereogenic center with (R)- or (S)-configuration.

LCs having three-ring aromatic mesogen cores tend to show the LC state at high temperatures. In fact, the CLCs exhibit a mesophase in the temperature range of 78–137°C. This temperature range is suitable for the Migita-Kosugi-Stille polycondensation, which often requires higher reaction temperatures than 60°C.[12–15]

Synthesis of Monomer

Scheme 2 shows the synthetic route for 2-dibromo thiophene-3-carboxylic acid 1-methyl heptyl ester (mono1). Mono1 was synthesized from 2-dibromo thiophene-3-carboxylic acid and (S)-2-octanol via the Mitsunobu reaction, in which the S_N2-type Walden inversion (Mitsunobu inversion) occurs. The chiral center in (S)-2-octanol was converted into (R)-configuration without racemization. The chemical structure of mono1 was confirmed with ^{1}H-NMR and MALDI-TOF MASS. The specific optical rotation for mono1 was estimated to be −15.49.

^{1}H-NMR for mono1 (400 MHz, CDCl$_3$, δ from TMS): δ 7.34 (s, 1 H), 5.09 (sext, 1 H, J = 6.4 Hz), 1.74−1.28 (m, 13 H), 0.88 (t, 3 H, J = 6.8 Hz). MALDI-TOF MASS: calculated for $C_{13}H_{18}Br_2O_2S$, 398.15; found m/z = 398.98.
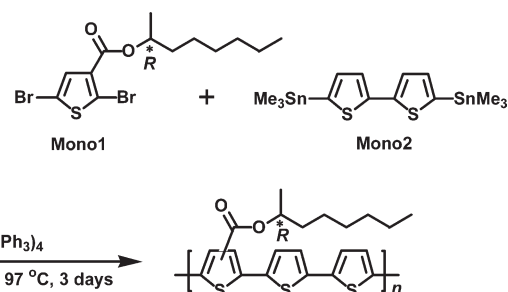
Synthesis of Polymer

Scheme 1 shows Migita-Kosugi-Stille polycondensation reaction between mono1 and 5,5′-bis(trimethylstannyl)-2,2′-bithiophene (mono2) by using the Pd(0) catalyst in toluene or the CLCs.

Poly1. (R)-LC (0.61 g, 1.37 mmol) was added to a Schlenk tube and maintained at 97°C. At that temperature, an iridescent color due to selective reflection of the CLC phase was visually confirmed. Subsequently, mono1 (0.0444 g, 0.111 mmol), mono2 (0.0543 g, 0.110 mmol), and Pd(PPh$_3$)$_4$ (1.0 mg, 0.9 × 10^{-3} mmol) were dissolved in (R)-LC, and stirred at 97°C. After 17 h, the reaction mixture was dissolved in a minimal amount of chloroform, and the solution was poured into a large amount of acetone. After stirring for 3 h, the supernatant was removed by decantation. The washing procedure was carried out again to remove the CLC molecules, low-molecular-weight oligomers,
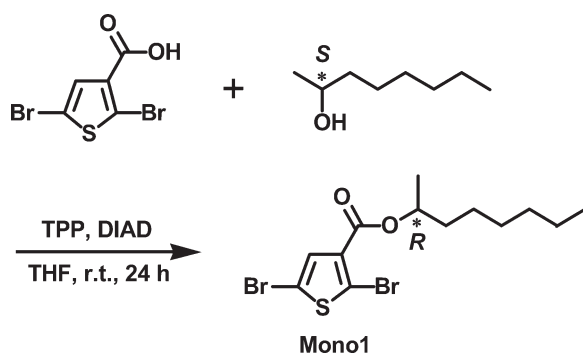
Scheme 2. Synthetic route for mono1. TPP, triphenylphosphine; DIAD, diisopropyl azodicarboxylate; THF, tetrahydrofuran.

Polymer	Monomer	Reaction medium
Poly1	Mono1 (R)-config.	(R)-LC
Poly2	Mono1 (R)-config.	(S)-LC
Poly3	Mono1 (R)-config.	Toluene

Scheme 3. Synthesis of the polymers.

and palladium dusts. Then, the residue was washed in methanol and dried in vacuum to yield poly1 as a red solid (0.0164 g, yield = 37%).

Poly2. Poly2 was synthesized under the same condition used for the preparation of poly1. Quantities used: (S)-LC (0.60 g, 1.34 mmol) mono1 (0.0444 g, 0.111 mmol), mono2 (0.0554 g, 0.112 mmol), and [Pd(PPh$_3$)$_4$] (1.1 mg, 1.0 × 10^{-3} mmol). Poly2 was obtained as a red solid (0.0187 g, yield = 42%).

Poly3. A solution of mono1 (0.0444 g, 0.111 mmol), mono2 (0.0551 g, 0.113 mmol), and Pd(PPh$_3$)$_4$ (1.1 mg, 1.0 × 10^{-3} mmol) in toluene (1 mL) was refluxed at 97°C. After 17 h, the solution was dissolved in a minimal amount of chloroform, poured into a large amount of acetone, and stirred for 3 h. The supernatant was removed by decantation, and the wash procedure in acetone was carried out again. The residue was washed in methanol and dried in vacuum to yield poly3 as a red solid (0.0271 g, yield = 60%).

Gel permeation chromatography (GPC) relative to polystyrene standards was carried out to estimate the molecular weight of the polymers. The number-average molecular weights (M_n) of poly1, poly2, and poly3 range from 2800 to 3700. The weight-average molecular weights (M_w) of poly1, poly2, and poly3 range from 3400 to 4400. These polymerization results are summarized in Table I.

The synthetic yield of poly3 (prepared in toluene) is the highest of the three polymers. This may be due to the higher viscosity of the CLC media compared with that of toluene, which reduces the reactivity of polymerization reactions for poly1 and poly2. Furthermore, the low-molecular-mass fractions of poly1 and

Table I. Polymerization Results

Polymers	M_n[a]	M_w[a]	M_w/M_n[a]	Yield (%)
Poly1	3300	4100	1.25	37
Poly2	3700	4400	1.20	42
Poly3	2800	3400	1.22	60

[a]Polystyrene standard.

poly2 were removed by purification, resulting in the low polymerization yield.

RESULTS AND DISCUSSION

Infrared Absorption Spectra

Figure 1 shows IR absorption spectra for (R)-LC, poly1, poly2, and poly3. All the polymers exhibit the same signal in the IR spectra. This indicates that the polymerization reactions in the CLC media proceeded as well as that in toluene. Poly1 and poly2 show no absorption at 1250 and 1725 cm^{-1} due to C=O stretching of (R)-LC. Poly3 shows small signal at 1250 cm^{-1}; however, this signal is not related to (R)-LC because poly3 was prepared in toluene. The absorption band at 1250 cm^{-1} might depend on the aggregation structure. The IR result suggests that CLCs were removed from the polymers after the purification.

Ultraviolet−Visible Absorption and Circular Dichroism Spectra

Figure 2 shows UV–vis absorption and CD spectra for poly1 ($5.25 \times 10^{-5}M$, calculated with molecular repeat unit, MRU), poly2 ($5.15 \times 10^{-5}M$, MRU), and poly3 ($4.94 \times 10^{-5}M$, MRU) in CHCl$_3$ solutions. The polymers show the same absorption band in the UV–vis. On the other hand, the CDs of the polymers show different spectral shapes. The polymers display the CD signals at short wavelengths (positive signal at ~400 nm and negative signal at 300 nm; poly3 shows no clear signal at 300 nm). Poly2 shows a positive broad band at long wavelengths, whereas poly1 shows weak signal and poly3 a negative signal at the long wavelengths. Note that the matrices (R)-LC and (S)-LC show positive and negative CD bands at ~310 nm, respectively.

In our previous study, we have reported that polymerization of achiral monomers in CLCs ((S)-LC and (R)-LC) yield several pairs of chiroptically active polymers which exhibited comple-

Figure 2. UV–vis (lower) and CD (upper) spectra for the poly1, poly2, and poly3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mentary mirror-image CD signals without chiral centers or axial chirality in the primary structure. This chiroptical activity is produced by transcription of structural chirality from the CLC matrix. The resultant polymers form chiral π-stacking similar to that of cholesteric LCs.

In this study, the polymers having the chiral substituent show optical activity at the π–π* transition of the main chain, indicating that the polymers have chiroptical activity with a main chain twisted in a predominant direction (secondary structure). Poly3 displays signals in the CD without the assistance of transcription of the structural chirality from the CLC medium. Especially, poly2 (the polymer prepared from monomer ((R)-configuration) in CLC ((S)-configuration) exhibits an intense signal in the CD in contrast to that of poly1 and poly3.

A chiral stacking model for polythiophenes with chiral substituent prepared in isotropic solvent has been proposed.[16] In this case, the polymers spontaneously form chiral aggregation based on intermolecular interaction. According to this model, poly3 (polymerization of the chiral monomer in toluene) may also form a structural chirality with spontaneous aggregation because poly3 has central chirality in the substituent. Therefore, structural chirality of poly2 is produced both by the spontaneous chiral aggregation and by the transcription from CLC medium. These two driving forces provide the polymer with an intense CD signal. On the other hand, the polymer (poly1) from the monomer with (R)-configuration prepared in CLC with (R)-configuration shows weak intensity in the CD compared with that of poly2 and poly3, indicating that the transcription from the cholesteric medium was not performed smoothly.

DSC

Figure 3 shows DSC results for polymerization mixtures of poly1 and poly2 before and after polymerization. The scanning rate of the DSC measurements was 10°C/min. Before polymerization, the reaction mixtures consist of the CLC and the
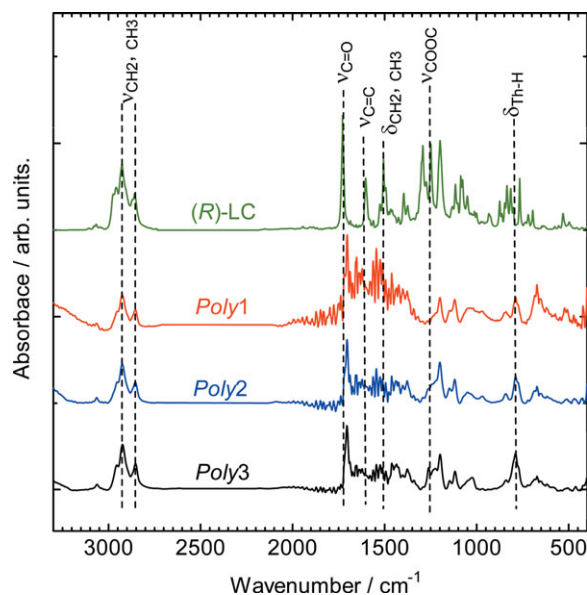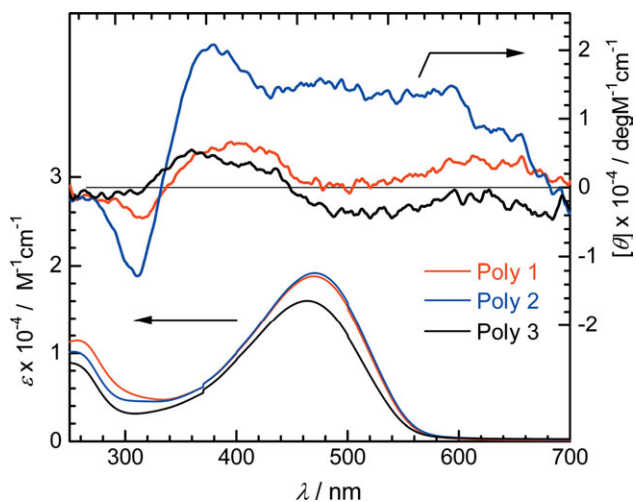

Figure 1. Infrared (IR) absorption spectra for the (R)-LC, poly1, poly2, and poly3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
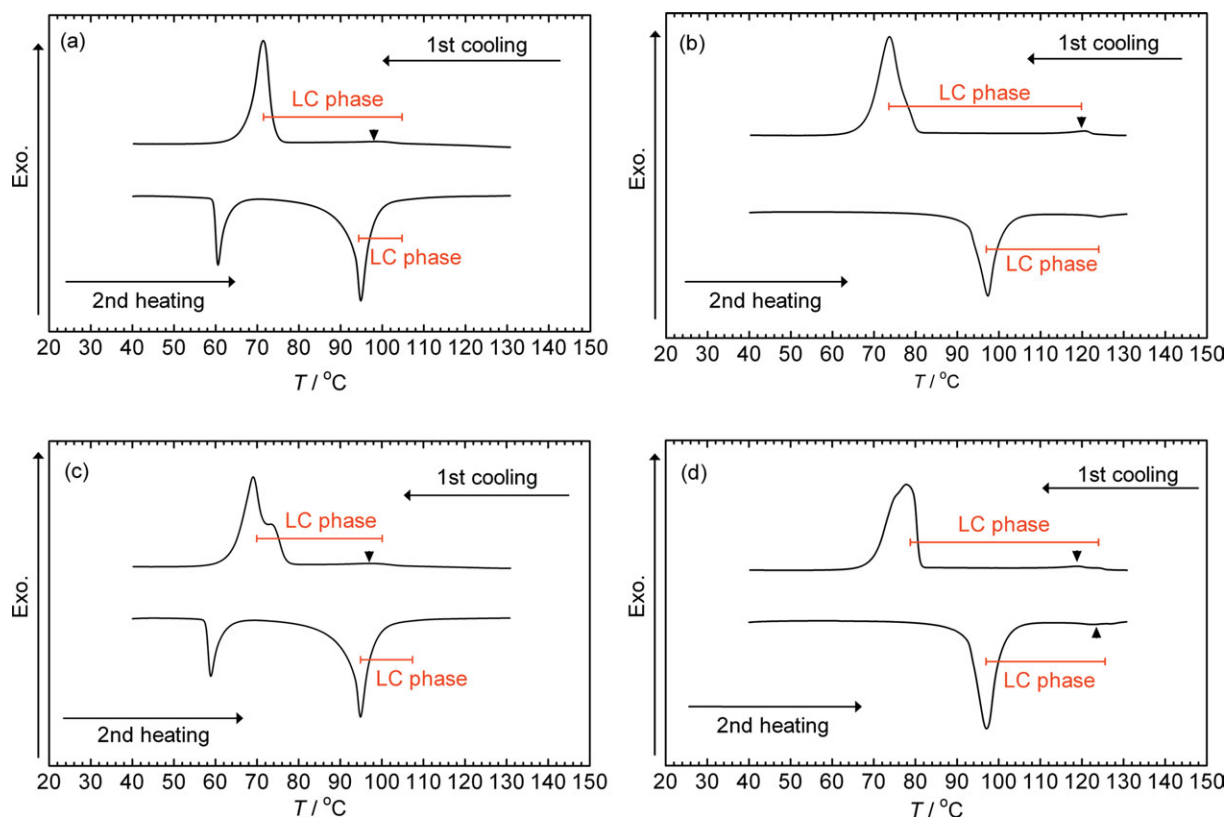
Figure 3. (a) DSC results of the reaction mixtures of poly1 before polymerization. (b) Poly1 after polymerization. (c) Poly2 before polymerization. (d) Poly2 after polymerization. Small arrows indicate peaks and troughs in the curves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

monomers. After polymerization (before purification), the mixtures consist of the CLC, the resultant polymer, and the catalyst. All the reaction mixtures for poly1 and poly2 show thermotropic mesophase at the polymerization temperature (cooling process, 97°C). These results confirm that the polymerizations were carried out in the cholesteric phase of the CLC materials ((R)-LC and (S)-LC).

Polarizing Optical Microscope Observation for Polymerization Media

Figure 4 shows POM images for the polymerization mixture at 97°C in the cooling process. At 97°C, all the polymerization mixtures show cholesteric phase. These results support that the (R)-LC and (S)-LC play the role of LC polymerization media. Furthermore, the mixtures before polymerization of both poly1 and poly2 exhibit the platelet texture of blue phase with stripes (blue phase I).

However, polymerization in the blue phase was not successful. In this study, although the blue phase is found at 97°C for the polymerization mixture before polymerization, the mixtures after polymerization do not exhibit the blue phase at the polymerization temperature. The mixture was consistently stirred (78 rpm) during the polymerization because reaction temperature should be maintained at the LC range with stirring required for polymerization to occur in the viscous LC. Unfortunately, the blue phase was not maintained under such

conditions. Polymerization in blue phase should be possible if a LC system showing a blue phase stable against external forces such as shear stress is developed, as a future project.

The monomer with (R)-configuration in the substituent may have good affinity with the CLC medium with (S)-configuration. The present polymerization with chiral-chiral interaction between the monomer and the CLC matrix in the polymerization process may involve repulsion (chiral separation) and affinity in chirality. In this research, effective chirality transcription of the monomer from the CLC with the opposite absolute configuration from the monomer in the polymerization was confirmed. This mechanism of chirality transcription may be related with the double gear model. One gear sandwiched between two gears rotates in the opposite direction against the two gears. If the monomer grows between CLC molecules with twist, the polymer would be propagated with opposite helical direction against the CLC between the CLC molecules. However, the detailed process involves chiral–chiral interactions is unclear at present.

Plausible Helical Model

To explain the result thus obtained, we propose a "twisted main chain helical stacking model" for the intense signal of poly2 in the CD. Possible forms of chiral π-stacking: (a) the main chain helical form and (b) the demonstration image of geometric
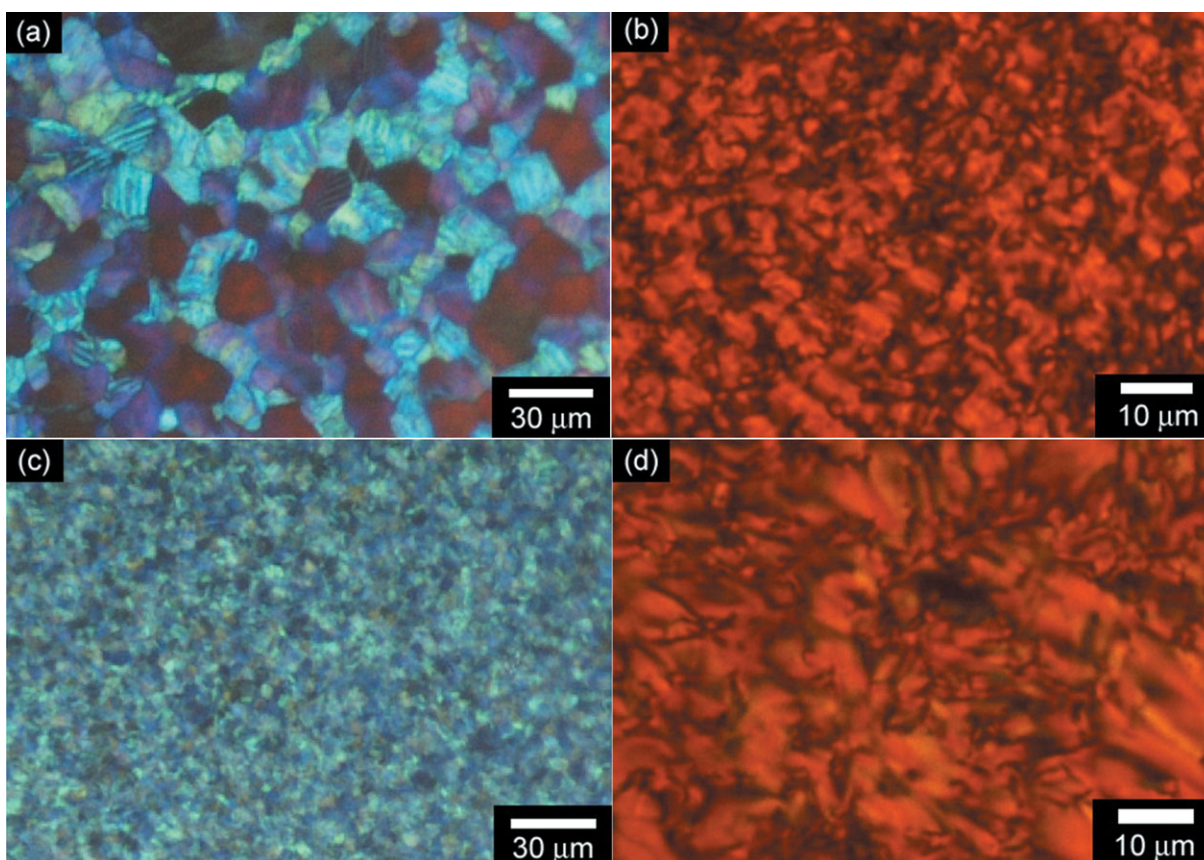
Figure 4. (a) Polarizing optical microscopic images of the reaction mixtures of poly1 before addition of catalyst showing blue phase. (b) Poly1 after polymerization. (c) Poly2 before addition of catalyst showing blue phase. (d) Poly2 after polymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

arrangement by using copper sheet (c) are shown in Supporting Information Figure S1. Main chain helicity and helical aggregation have been proposed.[16] We applied intermain chain helicity (interhelical structure) and intramain chain helicity (intrahelical structure) for the present polymers. The main chains are twisted predominantly in one direction and the main chains are stacked in the helical manner.

The long, thin copper sheets with left-handed twist are never stacked with left rotation and not arranged like a flower [Supporting Information Figure S1(c)]. The model implies that the left twisted main chain seems to be incompatible with formation of a left-helical π-stacking three-dimensional (3D) structure due to steric hindrances between the main chains, resulting in the loss of helical structure. However, a combination of left-twisted main chains and a right interhelicity (opposite direction) has a good affinity between neighboring main chains for formation of the stereostructure. As a result of these considerations, good structural chiral induction can occur for poly2 (from the monomer of (*R*)-configuration) prepared in (*S*)-LC at molecular level. The one-sided stacking process is schematically indicated in Supporting Information Figure S2, as a supplementary explanation of the helical model.

This model can explain the structural chirality (phase chirality) of the cholesteric medium for poly2, which functions for forma-

tion of the 3D chiral structure as a ternary structure in the polymerization process. The structure is maintained by π-stacking (chiral π-stacking) between main chains even after washing. Although the molecular form and aggregation state need to be visually evaluated in the future, the model can explain this phenomenon at the present stage.

CONCLUSIONS

Absolute configuration of the side chain in the monomer affects formation of chiral π-stacking structures produced by transcription from the CLC matrix as a 3D-chiral continuum in the polymerization process. The result in this research implies that affinity of the growing species (chiral monomer) in the transcription mechanism may be related to biological reactions at enzymes because certain chiral 3D structures of enzymes produce biological polymers with one-handed helical structure (starch and proteins). Furthermore, amino acids are L-form, except for some of the D-amino acids such as D-serine (in the brain) where D/L labeling is based on glyceraldehydes. However, D-glucose with the opposite configuration is expressed for biological reactions. From this viewpoint, the combination of absolute configuration between molecules in chemical reaction is important for production and consumption of chiral molecules for biological reactions. Transcription of chirality in asymmetric

synthesis by using chiral liquid crystals that we propose in polymer reactions can be one of the methods for evaluation of asymmetric reactions in organisms.

Polymerization in chiral media provides chiral polymers in environmentally asymmetric reactions. Here, optical activity of the resultant polymer is clearly confirmable with the CD in the visible range because chirality of the resultant polymers is enhanced by polymer effects, allowing a discussion of the transcription process in the chiral medium. Chiral aggregation can be applied for preparation of optically functional thin films. This research may provide a basis for further study of chiral aggregation chemistry.

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