



# Catalysis direction selective asymmetric polymerization in chiral liquid crystal medium

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### Highlights

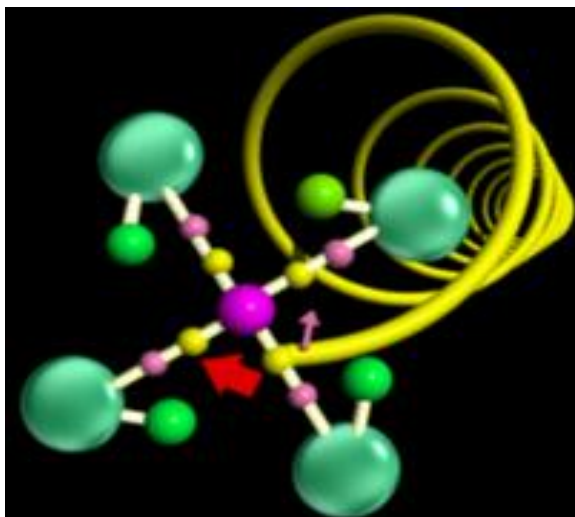
- Synthesis and characterization of a series of polyisocyanides.
- Polymerization in asymmetric liquid crystal.
- Preparation of chiroptically active polyisocyanides.
- Helical sense controllable polymerization.
- In situ ESR spectra of polyisocyanides.

## Catalysis direction selective asymmetric polymerization in chiral liquid crystal medium

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Catalysis Direction Selective Asymmetric Polymerization in Chiral Liquid Crystal Medium

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### ABSTRACT

A series of optically inactive aryl isocyanide derivatives were polymerized with an achiral

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nickel catalyst (Ni(II)Cl<sub>2</sub>) in a cholesteric liquid crystal (CLC) medium. The polymers synthesized from *ortho*-substituted phenyl isocyanide monomers in CLC phase show optical activity even though they have no chiral carbons. The Cotton effects of these polymers suggest that main chains of the polymers formed predominantly one-handed helical conformation. One-handed chiral environment in reaction state provided by CLC medium allows the formation of the polymers. The helical sense of the polymers is controllable by choice of (*R*)- or (*S*)-CLC as reaction solvent, though the monomer is same.

*Keywords*; Aryl isocyanide, Cholesteric liquid crystal, Helical polyisocyanide

## Introduction

Macromolecular chirality has drawn great interest across a broad range of biopolymers such as DNA [1] with double helix and proteins with  $\alpha$ -helix [2]. Constructing helical structure of synthetic polymer backbone is attractive for its potential use in biomimetic technology and prospective applications, such as asymmetric separation [3,4] and chirality sensing [5]. Polyisocyanides [6], polysilanes [7], and polyacetylenes [8] have been used as backbones of synthetic helical polymers. Helical structures in macromolecules are originated from isotacticity and atropisomerism of their structures.

Polyisocyanides are known to form unique helical structure with 4<sub>1</sub>-helix and have high stiffness due to their helical backbone [9]. Poly(aryl isocyanide)s with a bulky side group form a stable helical conformation even in solution. The first determination of the occurrence of enantiomeric helices for polyisocyanides was proved by chromatographic separation of poly(*tert*-butyl isocyanide) into enantiomers [10]. Recently, determination of the structure for polyisocyanides has been performed by direct observation of the molecular shape by using atomic force microscopy (AFM) and vibrational circular dichroism (VCD) spectroscopy combined with density functional theory (DFT) calculation [11]. These one-handed helical polyisocyanides generally can be prepared either with chiral isocyanide monomers [12] or chiral catalysts [13]. In addition, induction of helicity in optically inactive poly(phenyl isocyanide)s by external chiral stimuli through acid–base interactions was also reported [14]. Helical structure of polyisocyanides can be stabilized with bulky substituents and intermolecular hydrogen bond formation. *Ortho*-substituted poly(aryl isocyanide)s with bulkiness can be a good example for consideration of the steric effect on the capability of the helical conformations [12,13]. Chiral poly(*ortho*-substituted aryl isocyanide)s from achiral isocyanide monomer derivatives have been synthesized by using nickel (II) complexes with a chiral amine ligands. The sterically hindered isocyanide monomers give rise to enantiomeric excess of one-handed helical forms in the initial stage of the propagation, because of the chiral amine coordinated to the nickel center.

Recently, we have reported synthesis of an optically active poly(1-naphthyl isocyanide) in a

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CLC medium with achiral Ni(II)Cl<sub>2</sub> catalyst [15]. During the polymerization reaction, the CLC medium acts as a “one-handed chiral organized matrix” consisting of chiral directors. This chiral matrix induces one-handed helical conformation in the polymer. Similar to enzymes in living cells, CLC phase exists in a certain temperature range and produce optical activity for polymers depending on excluded volume effect between monomers and the CLC molecules [16]. If the chiral induction to polymer can be assisted by polymerization in CLC phase, the result can open the possibility of polymerization in CLC, which performs a similar function like biological system. The helicity of the polymer is maintained by inter-lock function between laterally substituted naphthalene rings through  $\pi$ -stacking. In this study, a series of aryl isocyanide monomer derivatives with various substituents and substituted positions were polymerized with Ni(II)Cl<sub>2</sub> in complementary CLCs. The steric hindrance of the substituents arise the chiral induction during the polymerization. In addition, we examined vortex induction effect by polymerization in nematic liquid crystal (NLC) phase using racemic-CLC molecule [17]. The poly(aryl isocyanide)s thus obtained were investigated by ultra violet-visible (UV-vis) absorption, circular dichroism (CD), and infrared (IR) absorption spectroscopies.

## Experimental

### *Materials and instruments*

The commercially available reagents were received from Nacalai Tesque Co., Ltd., Aldrich, Kanto Chemical Co. and TCI chemicals and used without further purification. The common organic solvents such as dichloromethane and tetrahydrofuran (THF) were distilled and handled in a moisture-free atmosphere. The purification of the newly synthesized compounds was performed by column chromatography on silica gel (Silica gel 60 N). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the compounds were recorded using ECS 400 spectrometer with CDCl<sub>3</sub> as the deuterated solvent and tetramethylsilane (TMS) as the internal standard. The chemical structure and optical property of a series of polymers were confirmed by the IR spectroscopy (Jasco, FT-IR 500 spectrometer using KBr method), CD spectroscopy (Jasco, J-720 spectrometer) and UV-vis spectroscopy (Jasco, U-3500 spectrophotometer). ESR measurement of the solid polymer sample packed into a 5 mm quartz tube was carried out using Bruker EMX-T ESR Spectrometer.

### *Synthesis of liquid crystal solvents*

An enantiomeric pair of (*R*)- and (*S*)-CLC was prepared according to the previously reported method [18]. The (*R*)- and (*S*)-CLC consist of a three-ring core with chiral alkyl chains that have (*R*) or (*S*) configurations. A racemic LC was also synthesized ((*R,S*)-8BpB2). Fig. 1 shows the chemical structure of the (*R*)-CLC, (*S*)-CLC, and (*R,S*)-8BpB2. Their liquid crystallinities were confirmed by differential scanning calorimetry (DSC) and polarizing

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optical microscopy (POM). The (*R*)- and (*S*)-CLC exhibit a CLC phase at the temperature range from 78 °C to 138 °C. In addition, (*R,S*)-8BpB2 shows a NLC phase at the temperature range from 75 °C to 140 °C.

#### *Synthesis of aryl isocyanide monomers*

2-Naphthyl isocyanide (**1**) was purchased from Aldrich. 2-Phenylisocyno acetate (**2**) and 2-phenylisocyno isobutyrate (**5**) were prepared by base-promoted ring-opening reaction of benzoxazole [19]. 2-Methoxyphenyl isocyanide (**3**), 3-methoxyphenyl isocyanide (**4**), and 2,6-dimethoxyphenyl isocyanide (**6**) were prepared according to the method described in the literature [20,21].

#### *Polymerization*

Several polymerizations were performed in CLC, NLC, and isotropic phases of LC media (Fig. 1). Polymerization in CLC phase (100 °C) of the (*R*)-CLC medium gave poly-**1r**, poly-**2r**, poly-**3r**, poly-**4r**, poly-**5r** and poly-**6r**, while the (*S*)-CLC medium afforded poly-**2s** and poly-**3s**. Polymerization of poly-**3n** was carried out in NLC phase (100 °C) of the (*R,S*)-8BpB2 reaction mixture. Poly-**3i** prepared in isotropic phase (140 °C) of the (*R*)-CLC medium (Scheme 1). A typical procedure is described as follows. (*R*)-CLC, (*S*)-CLC, or (*R,S*)-8BpB2 (500 mg) as reaction solvents were placed in a Schlenk tube. After heated up to 150 °C, the reaction solvents were cooled to 100 °C and 140 °C to exhibit LC and isotropic phases, respectively. Then, the aryl isocyanide monomers (20 mg) and NiCl<sub>2</sub> (1.0 mg) were added to the solvents. The reaction mixtures were stirred at the rate of 72 rpm at 100 °C and 140 °C. After 24 h, the reaction mixtures were cooled to 0 °C, and poured into 80 mL of acetone and stirred for 4 h. The precipitates were collected by centrifugation at 15,000 rpm for 20 min. This procedure was repeated with acetone and methanol to remove monomers, catalysts, LC, and low molecular weight reactant. The precipitates were then collected and dried under vacuum to afford the desired polymers (**1–4**) as a green-yellow powder. Poly-**5r** and poly-**6r** could not be purified because they gave only acetone-soluble fractions.

## **Results and discussion**

#### *Liquid crystallinity of reaction mixture*

Liquid crystallinity of the LC media was examined by DSC and POM. Fig. 2 shows DSC curves for the CLC reaction mixture of poly-**3r** after polymerization. These DSC curves indicate that the reaction mixture exhibited CLC phase in the temperature range of 98–138 °C. The POM images of several LC reaction mixtures shown in Fig. 3. Fig. 3 (a, c, e, g, i, k, and m) shows the POM images of the reaction mixture containing monomers, catalysts, and LC solvent (before polymerization). Panels (b, d, f, h, j, l, and n) of Fig. 3 shows the POM images

of the reaction mixture containing monomers, polymers, LC solvent, and low molecular weight reactant (after polymerization). Fig. 3 (a–f and k–n) suggests that both the reaction mixture displayed Grandjean texture typically observed in CLC phase. The reaction mixtures of poly-**3n** showed a typical Schlieren texture of NLC phase (g and h in Fig. 3). The DSC curves and POM images support the fact that the polymerization reaction at 140 °C was performed in isotropic phase of the (*R*)-CLC medium (i and j in Fig. 3). Polymer fractions of higher molecular weight which were insoluble in the LC medium were observed as insoluble green masses in the reaction mixture after reaction for 24 h (b, d, f, h, j, l and n in Fig. 3). Besides, the liquid crystallinity of the reaction mixture was monitored by visual observation. The selective light reflection derived from CLC phase was confirmed in the (*R*)- and (*S*)-CLC media at 100 °C (before and after polymerization). The transparent brown color of the CLC medium at 140 °C both before and after polymerization support the isotropic phase of the reaction mixture. These results indicate that the entire polymerization reaction was performed in the corresponding LC phases of the LC media.

### GPC

The molecular weights were evaluated with gel permeation chromatography (GPC) relative to polystyrene standard (eluent: THF). Polymerization results are summarized in Table 1. The number-average molecular weights ( $M_n$ ) of poly-**1r** and poly-**4r** were 10,000 and 11,400. The  $M_n$  of poly-**2r**, poly-**2s**, poly-**3r**, poly-**3s**, poly-**3n**, and poly-**3i** were lower than that of the other polymers ( $M_n = 1800–3500$ ). This is because the polymers were partially soluble in THF, and only the THF soluble parts of the polymers were measured with GPC. The insoluble part in THF may consist of high molecular weight fraction. Poly-**3r** was more soluble than poly-**3n** (by visual observation). This may be attributed to the difference of conformation and aggregation of the polymers. Poly-**3i** gave a lower molecular weight than that of poly-**3r**, poly-**3s**, and poly-**3n** due to well-known thermal rearrangement of isocyanides to trimers and nitriles [22]. Poly-**5r** was not isolated by precipitation with acetone due to the low molecular weight fraction. Therefore, the polymerization mixture of poly-**5r** was injected directly into the GPC. 2,6-Dimethoxyphenyl isocyanide (**6**) did not polymerize because of its large steric hindrance.

### IR

Fig. 4 shows IR spectra of (*R*)-CLC, monomer **1–4**, and poly-**1r**, poly-**2r**, poly-**3r**, poly-**3n**, poly-**3i**, and poly-**4r** obtained by using KBr method. A broad absorption band (2840–3100  $\text{cm}^{-1}$ ) is due to C–H stretching. Each monomer has a common absorption band at 2125  $\text{cm}^{-1}$  ascribed to  $\text{C}\equiv\text{N}$  stretching. The absorption band of the polymers display no  $\text{C}\equiv\text{N}$  stretching, while they show  $\text{C}=\text{N}$  stretching bands (1637–1648  $\text{cm}^{-1}$ ). This indicates that polymerization of the monomers afforded  $\sigma$ -conjugated polyisocyanide backbones. Furthermore, complete

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removal of the LC media from the polymers was confirmed by the absence of the C=O stretching absorption band due to the LC molecule ( $1730\text{ cm}^{-1}$ ) on the all spectra. These results demonstrated that the all polymerization was successfully performed in the LC medium.

### *Optical activity*

Fig. 5 shows CD and optical absorption spectra of poly-**1r**, poly-**2r**, poly-**2s**, poly-**3r**, poly-**3s**, poly-**3n**, poly-**3i** and poly-**4r** in chloroform solution. The polymers synthesized in CLC phase (poly-**2r**, poly-**2s**, poly-**3r** and poly-**3s**) exhibited mirror-image Cotton effects, respectively around 400 nm due to the  $n-\pi^*$  transition of imino chromophores. The results suggest these polymers have predominantly one-handed helical conformations. The CD signal of the polymers prepared in (*R*)-CLC display negative first and negative second Cotton effects. The polymers prepared in (*S*)-CLC show the opposite sign of the Cotton effects. Besides, no significant Cotton effect was observed for poly-**3n** and poly-**3i** which was polymerized in NLC and isotropic phase, respectively. This demonstrated that the rod-shaped LC molecules ((*R,S*)-8BpB2) did not lead to spontaneous chiral symmetry breaking by the stirring direction and stir speed. These suggest that the chiroptical activity of the polymers is controllable by choice of (*R*)- or (*S*)-CLC as the reaction solvent, even though the other conditions are the same. Furthermore, no significant Cotton effect was observed for poly-**1r** and poly-**4r** which have no *ortho*-substituted moiety in the side chain. This indicates that the bulkiness of the *ortho*-position is another essential trigger for imparting predominantly one-handed helical conformations to the polymer by polymerization in CLC medium. Consequently, we can conclude that the polymers synthesized from the *ortho*-substituted phenyl isocyanides in the CLC phase should show optical activity.

### *Effects of solvent and thermal changes on the conformation of poly-3r*

Fig. 6 shows CD and optical absorption spectra of poly-**3r** in various solvents. Poly-**3r** was well dissolved in *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO), while it was partially dissolved in THF and chloroform. The intensities of the CD bands in THF and chloroform solutions are lower than DMF and DMSO solutions. This suggests that the high molecular weight fractions were dissolved in the good solvents and also composed of predominantly one-handed helical conformations. The absorption bands around 400 nm in the absorption spectra show red shift in polar solvents (e.g. DMF and DMSO) compared to low polar solvents (e.g. THF and chloroform). This tendency is also observed for the CD spectra. In the CD spectra, intensity of  $n-\pi^*$  transition band (ca. 450 nm) is higher than that of  $\pi-\pi^*$  (ca. 270 nm) in THF, and chloroform solutions, while that is opposite in the case of DMF and DMSO solutions. The polarity of the solvents increases in the order of THF, chloroform, DMF,

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and DMSO [23,24]. The differences in the intensity of the Cotton effect in solution are due to conformational changes of poly-**3r** by changing solvents polarity.

To investigate thermal stability of polymer conformation, poly-**3r** in DMSO solution was subjected to multiple cycles of thermal heating (110 °C) and cooling (20 °C). Fig. 7 shows the change of CD intensities (456 nm) of the sample in multiple thermal cycles. Each value of the measurements was obtained after maintaining at each temperature for 20 min. The intensity was gradually decreased with heating from 20 °C to 110 °C, but this loss was mostly recovered by subsequent cooling from 110 °C to 20 °C. This reversible intensity change of the Cotton effect (456 nm) with thermal changes indicates the conformational transition of poly-**3r**. The helical pitch of poly-**3r** is longer at 110 °C than that of at 20 °C estimated from the CD measurement. Besides, the optical activity of poly-**3r** decreased gradually by repeating thermal cycles. This result demonstrated that predominantly one-handed helical conformation of poly-**3r** was gradually racemized by repeating thermal treatment.

#### *Stability of the helical structure after annealing in CLC*

Further investigation was carried out for thermal stability of poly-**3r** and association between helical structure of polymer and CLC medium. After polymerization reaction of monomer **3** in CLC phase at 100 °C for 1 day, the reaction mixture was heated to 140 °C to become isotropic phase and stirred for 1 day. Scheme 2 shows the procedure of the annealing and synthesis for poly-**3ri**. Poly-**3ri** was purified by the same procedure that of the other polymers. Polymerization results and IR spectrum of poly-**3ri** were similar to those of poly-**3s** and poly-**3r** (Table S1 and Fig. S5). Fig. 8 shows CD and optical absorption spectra for poly-**3ri** in chloroform solution. The CD spectrum of poly-**3ri** gave Cotton effect similar to that of poly-**3r**. This result clearly indicates that the predominantly one-handed helical conformation was maintained through the 24 hours annealing at 140 °C in isotropic phase of the (*R*)-CLC medium. Since poly-**3r** and poly-**3ri** exhibit similar CD spectra while poly-**3n** and poly-**3i** have no Cotton effect, the predominantly one-handed helical structure of the polymers was induced by the effect of the three-dimensional (3-D) one-handed helical structure of the CLC medium during polymerization.

#### *Effect of CLC and Liquid Crystallinity*

For the Ni(II) catalyzed polymerization of isocyanides, so-called “merry-go-round” mechanism was proposed [25]. Subsequently, the first structural characterization of a crucial intermediate for the polymerization of isocyanides with Ni(II) catalyst was experimentally demonstrated by Feiters et al. [26]. In these papers, chiral polyisocyanides were obtained by using a chiral solvent which contains amino groups. The amino groups act as nucleophile and react with the first unit of a isocyanide coordinated to the nickel center. As a result, chiral polyisocyanides were obtained due to the steric effect of the bulky chiral amine. On the



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contrary, chiral alcohols did not work for obtaining chiral polyisocyanides because of their lower reactivity than that of amino groups.

In this research, the CLC molecules which have no amino groups were used as the chiral solvent. During the polymerization reaction, no chiral molecules participate in the reaction routes. The results indicate that the chiral induction of poly-(**1-4**) by polymerization in a CLC medium was achieved due to the 3D one-handed helical structure of the CLC solvent. Fig. 9 shows a proposed mechanism for the polymerization of *ortho*-substituted aryl isocyanides in the CLC medium. The reaction starts from a square-planar nickel complex. Subsequent a nucleophile ( $\text{Cl}^-$  of  $\text{Ni(II)Cl}_2$ ) attack produces an activated complex. Then carbanion  $\text{C}^1$  has gained in nucleophilicity. The carbanion  $\text{C}^1$  can attack either the neighboring isocyanides on a coordinated isocyanide. Usually, the carbanion  $\text{C}^1$  attacks equally in probability on both sides of neighboring isocyanides,  $\text{C}^2$  and  $\text{C}^4$ . In the case of the *ortho*-group pointing one-direction,  $\text{C}^1$  preferentially attacks the less steric hindered side. In the Fig. 9,  $\text{C}^1$  predominantly attacks  $\text{C}^2$ . If the direction of *ortho*-group of phenyl isocyanide was regulated and stabilized by the CLC medium, the carbanion preferentially attacks on the one side of neighboring isocyanides in the propagation step, leading to the formation of the predominantly one-handed helical structure. On the contrary, aryl isocyanides possessing no *ortho*-substituents did not form such helical polymers due to less steric hindrance.

Aryl isocyanides with the appropriate steric hindrance at *ortho*-positions provide the conditions for the chiral induction by the polymerization in the CLC phase. This model can explain the helical induction of poly(1-naphthyl isocyanide) and poly(*ortho*-substituted phenyl isocyanide)s by the polymerization in the CLC phase. One-handed chiral environment of the CLC medium could support the one-direction polymer propagation, resulting formation of predominantly one-handed helical poly(aryl isocyanide)s as an atropisomer. In other words, the chiral environment regulates the direction of isocyanides in complexation and allows formation of helical structure with a good affinity for the polymers. This system can be referred to as field effective structure organized polymerization.

#### *Electron spin resonance measurements*

*In-situ* ESR spectra of poly-**3r** and poly-**3n** with vapor phase iodine doping were measured, respectively (Fig. S1 and S3). The polymers show a single isotropic Gaussian signal without hyperfine splitting. The ESR signal intensity of poly-**3r** and poly-**3n** initially increased with *in-situ* doping, then gradually decreased after 5 min and 8 min, respectively. The *g*-value, line width ( $\Delta H_{\text{pp}}$ ), and ESR intensity of the polymers were plotted as functions of doping time for 0–60 min (Fig. S2 and S4). The peak width was almost constant through the doping process. *g*-Value of the polymers increased slightly to ca. 2.0048 from ca. 2.0043 with heavy doping. Upon iodine doping, the intensity of the paramagnetic ESR signal increased with time, indicating that radical cations are generated by the doping process. In the next stage, the

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generation of dications decreases spin concentration of the polymers, resulting the decrease of the ESR intensity. This is a typical behavior of doping process with generation of radical cations and dications [27]. This experiment demonstrated iodine doping behavior of the polymers. The available evidence is considered. *g*-Value of the polymers is most consistent with formation of an iminyl radical [28]. The doping experiment exactly confirmed generation of doped *N*-atoms in the polyisocyanides molecular chains.

## Conclusion

Optically active poly(*ortho*-substituted phenyl isocyanide)s were prepared with achiral Ni(II)Cl<sub>2</sub> in CLC phases. Comparison of analogous poly(aryl isocyanide)s with no *ortho*-substituent suggests that the steric hindrance at the *ortho*-position is an important factor for providing the predominantly one-handed helical structure. Polymerization of monomer **2** and **3** in complementary CLC media revealed that helical sense of the polymers is controllable by choice of (*R*)- or (*S*)-CLC as reaction solvent. Conformational change of poly-**3r** was observed with solvents polarity and thermal treatment. In addition, the CD property of the sample was thermally reversible. The CD measurement of poly-**3ri** demonstrated the helical structure of poly-**3r** was stable even after annealing at 140 °C in CLC medium for 24 h. This implies that there is good affinity between the polymer and CLCs.

Appropriate molecular form and surrounded chiral environment proceed a new concept reaction of environment encouraging helical form propagation. This result indicates that metal catalyzed reaction with an aid of chiral environment affords chiroptically active polymer. The results in this research can be connected to biological reactions in the point of collaboration of the chiral environment for catalyst.

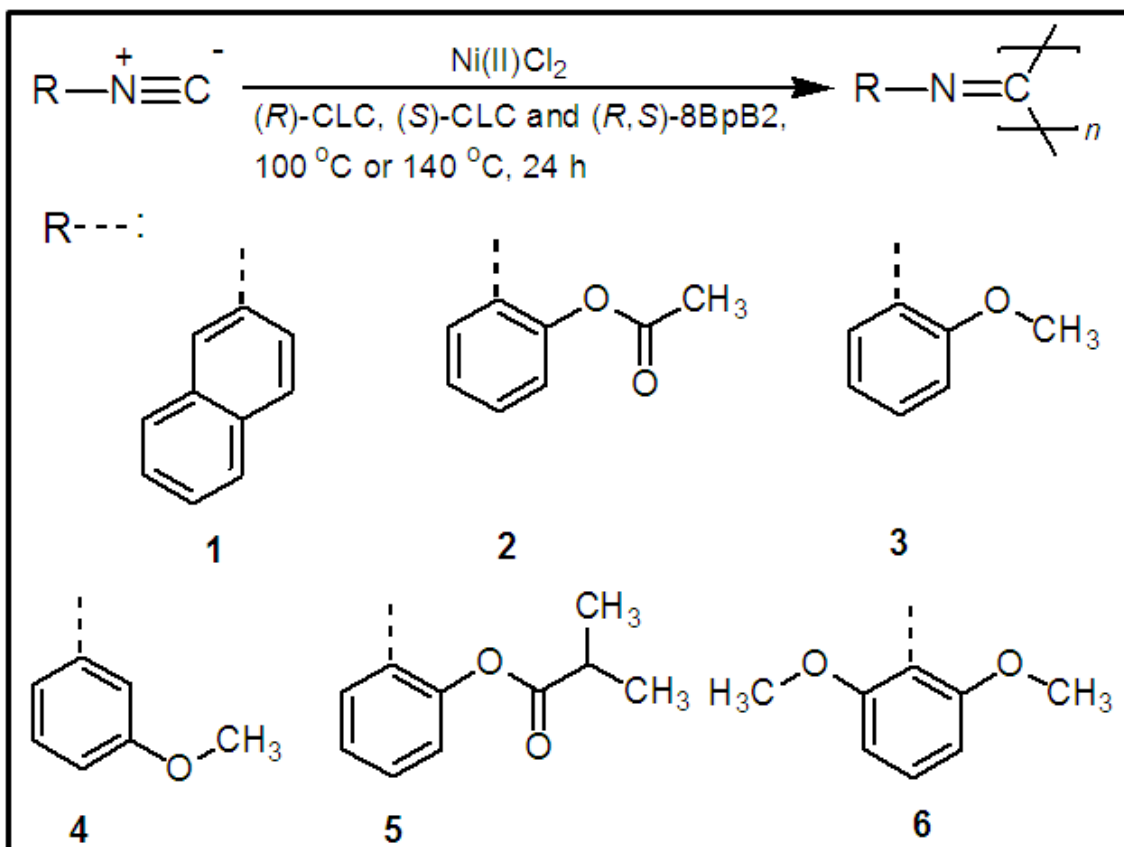
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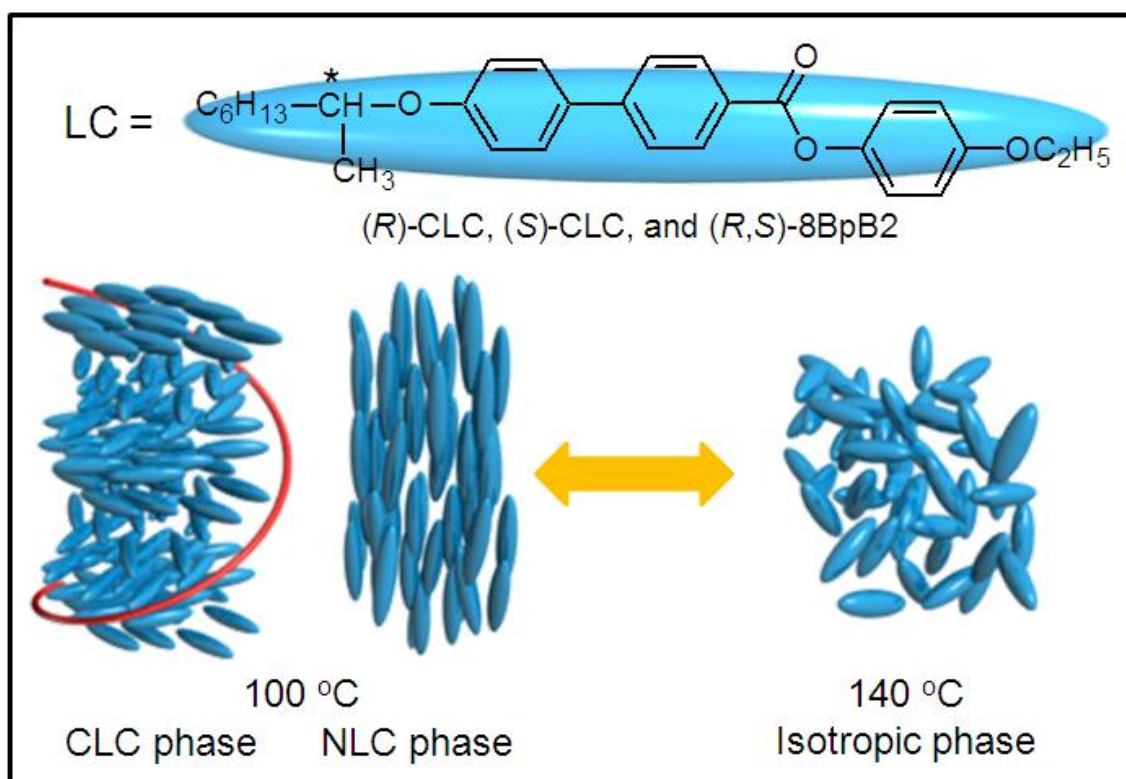
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**Scheme 1.** Polymerization of aryl isocyanides

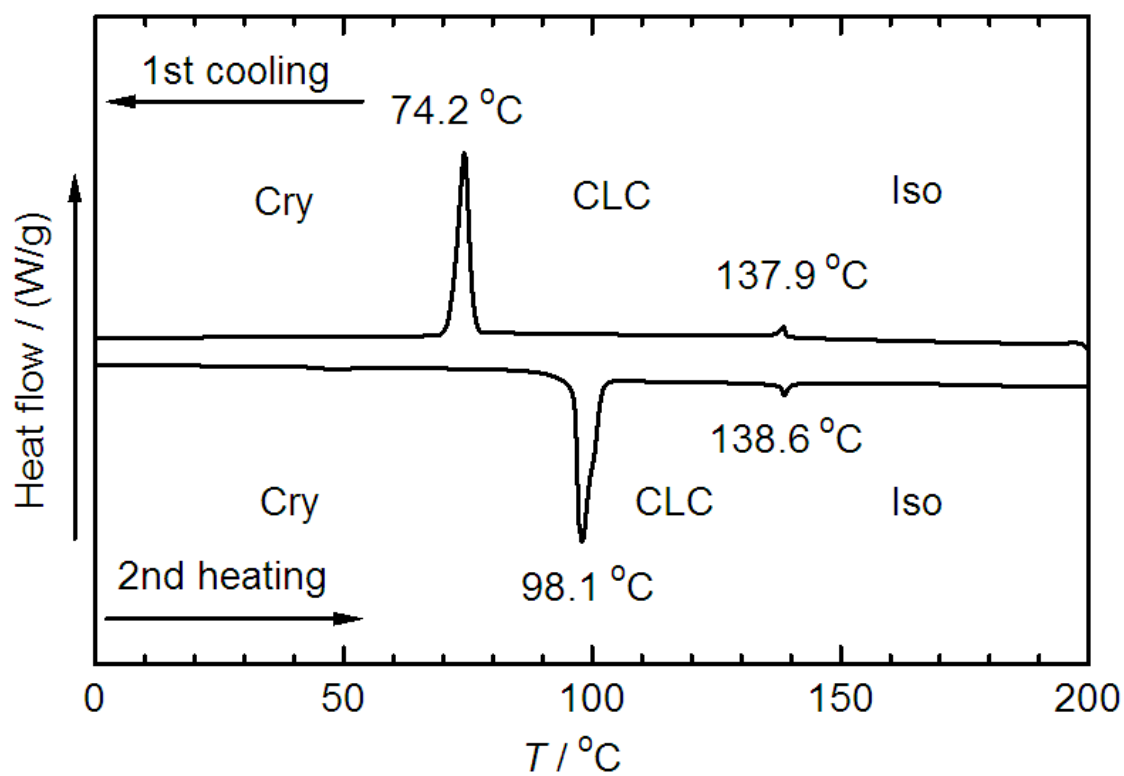


**Fig. 1.** Structural transformation of LC molecules accompanied by phase transition ((*R*)- and (*S*)-CLC and (*R,S*)-8BpB2 exhibit CLC and NLC phase at 100 °C, respectively).

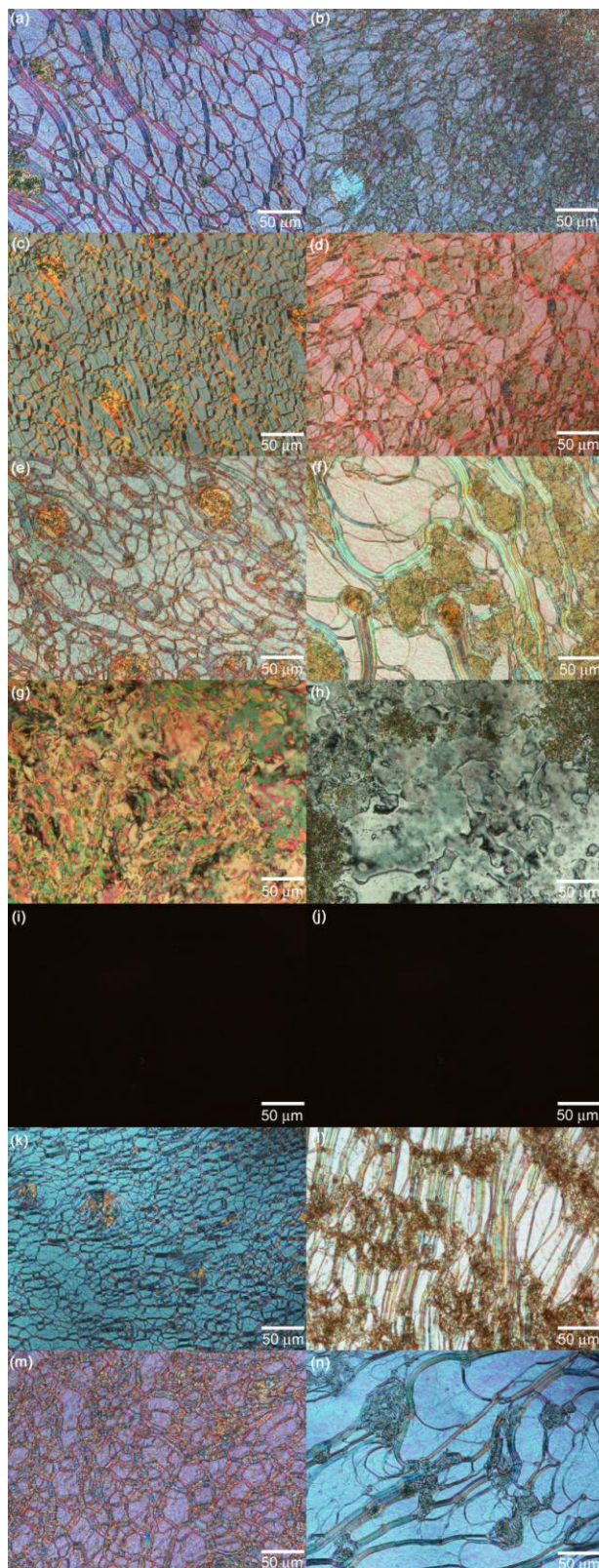
**Table 1.** Polymerization conditions and results.

Monomer	Polymer	Polymerization condition			$M_n^a$	$M_w^a$	$M_w/M_n^a$	Yield (%) <sup>b</sup>
		Solvent	Temp	Phase				
<b>1</b>	poly- <b>1r</b>	( <i>R</i> )-CLC	100 °C	CLC	10,000	11,800	1.2	55
<b>2</b>	poly- <b>2r</b>	( <i>R</i> )-CLC	100 °C	CLC	3,200	3,300	1	20
<b>2</b>	poly- <b>2s</b>	( <i>S</i> )-CLC	100 °C	CLC	3,500	4,200	1.2	35
<b>3</b>	poly- <b>3r</b>	( <i>R</i> )-CLC	100 °C	CLC	3,200	3,600	1.1	27
<b>3</b>	poly- <b>3s</b>	( <i>S</i> )-CLC	100 °C	CLC	3,300	4,200	1.3	30
<b>3</b>	poly- <b>3n</b>	( <i>R,S</i> )-8BpB2	100 °C	NLC	3,100	3,700	1.2	58
<b>3</b>	poly- <b>3i</b>	( <i>R</i> )-CLC	140 °C	isotropic	1,800	2,000	1.1	8
<b>4</b>	poly- <b>4r</b>	( <i>R</i> )-CLC	100 °C	CLC	11,400	20,200	1.8	34
<b>5</b>	poly- <b>5r</b>	( <i>R</i> )-CLC	100 °C	CLC	1,500	1,600	1.1	- <sup>c</sup>
<b>6</b>	poly- <b>6r</b>	( <i>R</i> )-CLC	100 °C	CLC	-	-	-	-

<sup>a</sup> Determined by gel permeation chromatography (GPC) and relative to polystyrene standards (eluent: THF). <sup>b</sup> Isolated yield of high molecular weight fraction. <sup>c</sup> Poly-**5r** could not be isolated from the CLC mixture due to the low molecular weight.

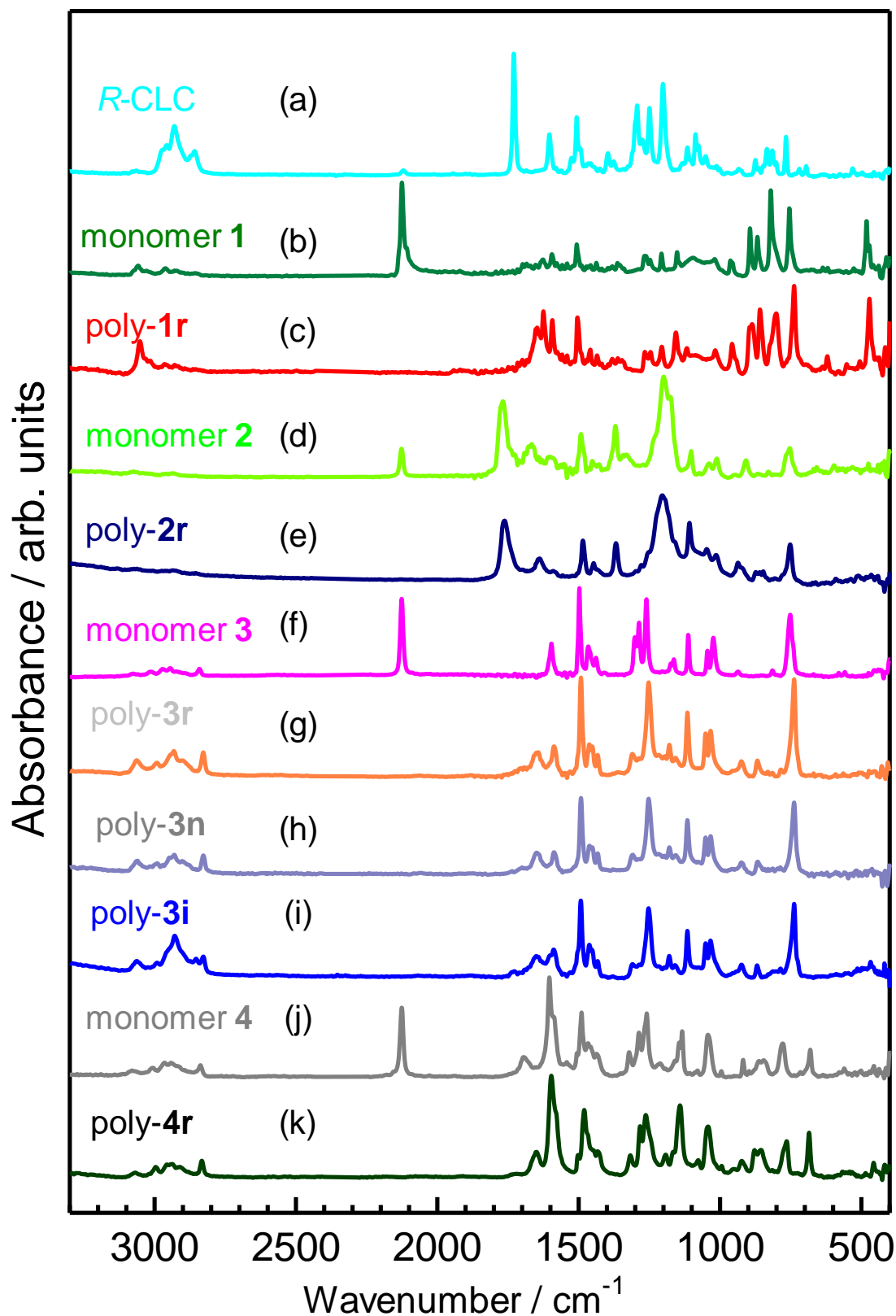


**Fig. 2.** DSC curves of the reaction mixture of poly-3r after polymerization.

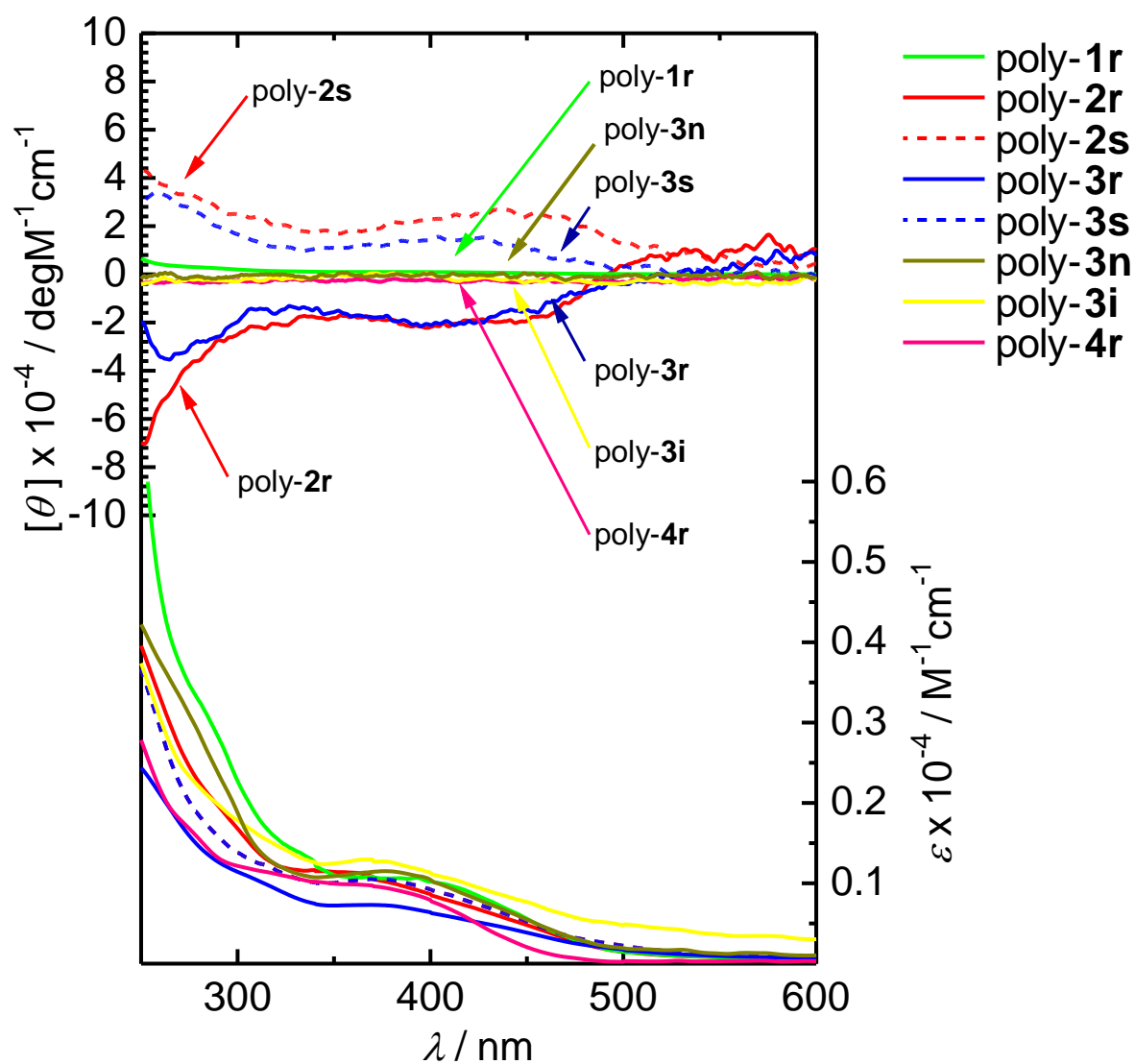


**Fig. 3.** Polarizing optical microscopy images of the reaction mixture of poly-1r (a), poly-2r (c), poly-3r (e), poly-3n (g), poly-4r (k), and poly-5r (m) at 100 °C and poly-3i (i) at 140 °C before reaction. LC solution for poly-1r (b), poly-2r (d), poly-3r (f), poly-3n (h), poly-4r (l), and poly-5r (n) at 100 °C and poly-3i (j) at 140 °C after reaction for 24 h.

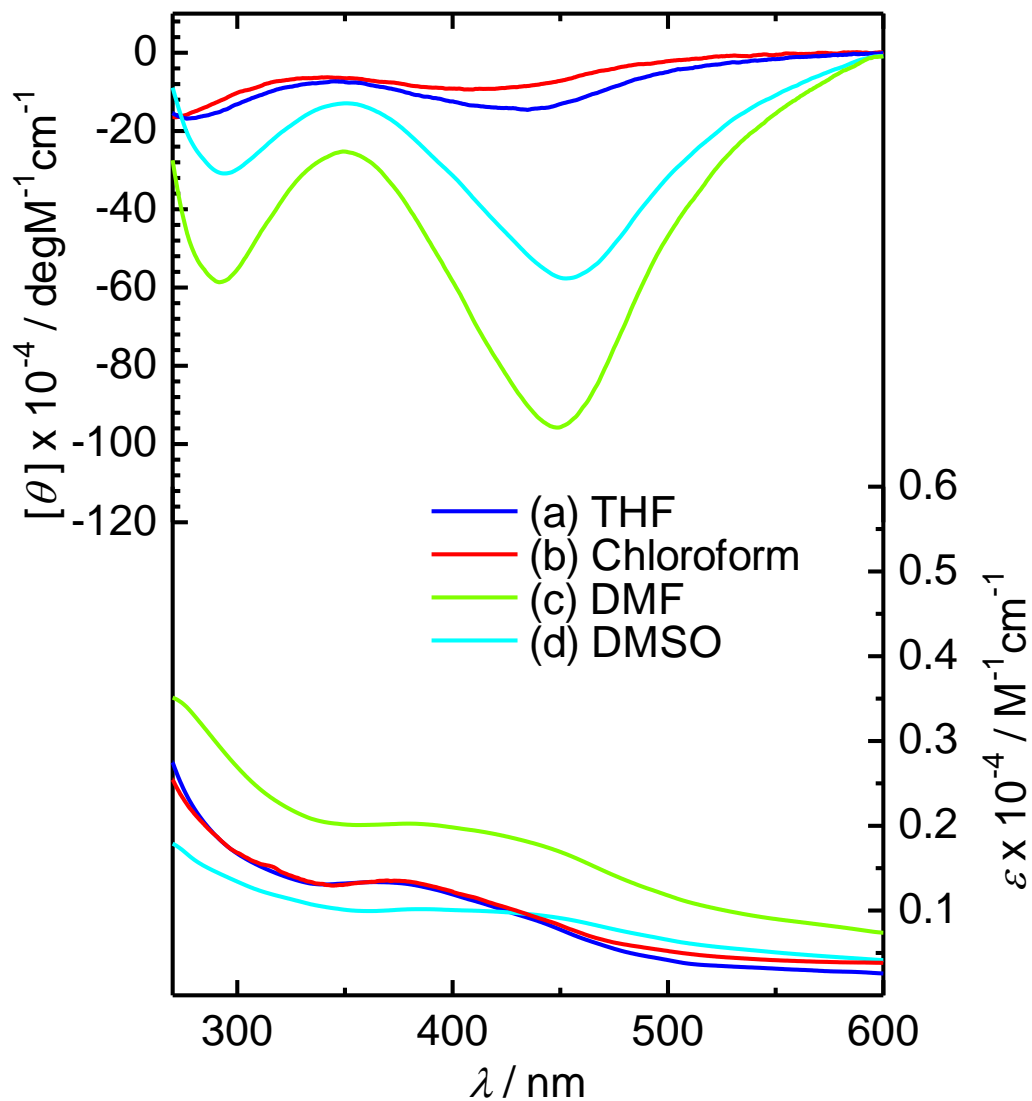




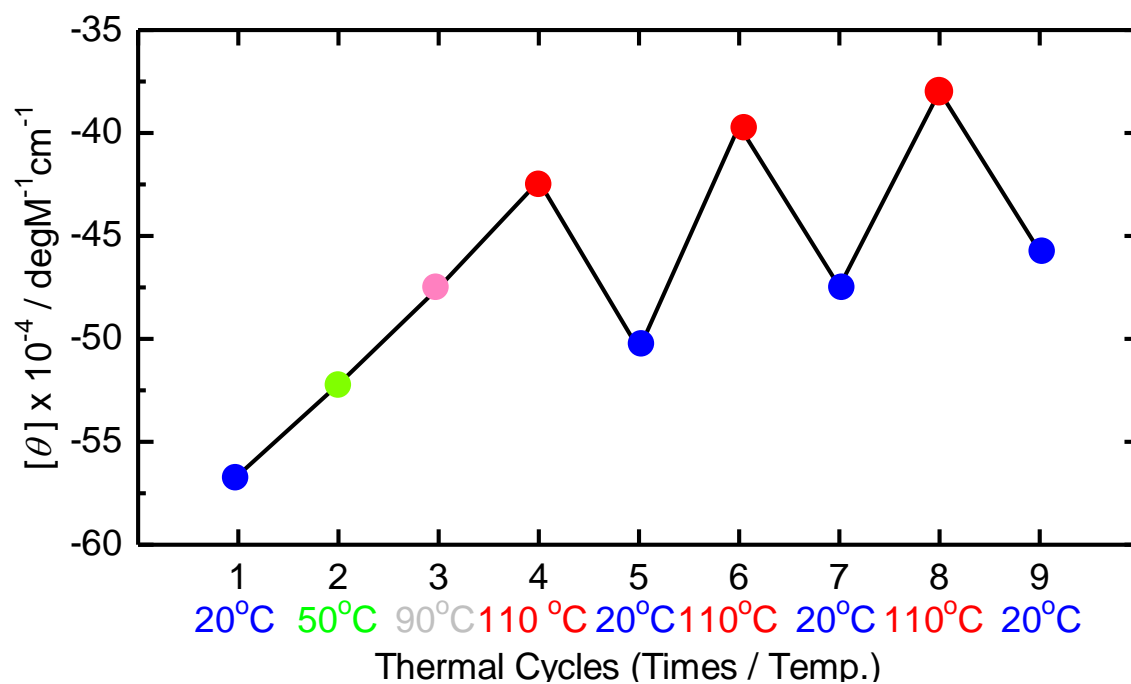
**Fig. 4.** IR absorption spectra of *R*-CLC (a), monomer 1 (b), poly-1r (c), monomer 2 (d), poly-2r (e), monomer 3 (f), poly-3r (g), poly-3n (h), poly-3i (i), monomer 4 (j), and poly-4r (k).



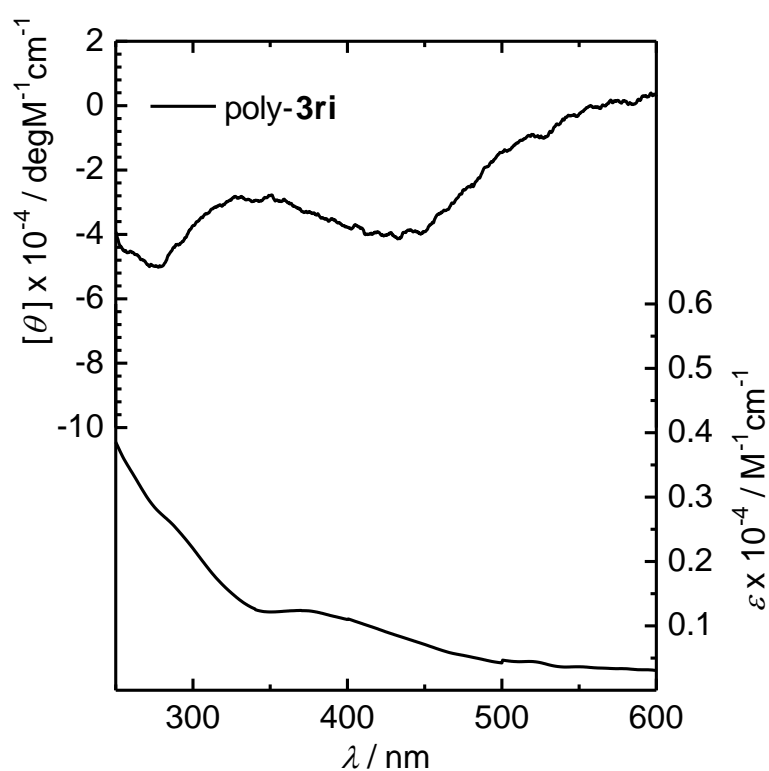
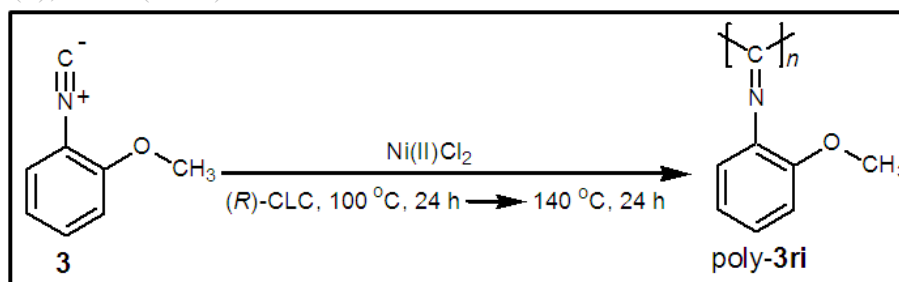
**Fig. 5.** CD (upper) and absorption (below) spectra for poly(aryl isocyanide)s in chloroform (0.02–0.03 mg/mL).



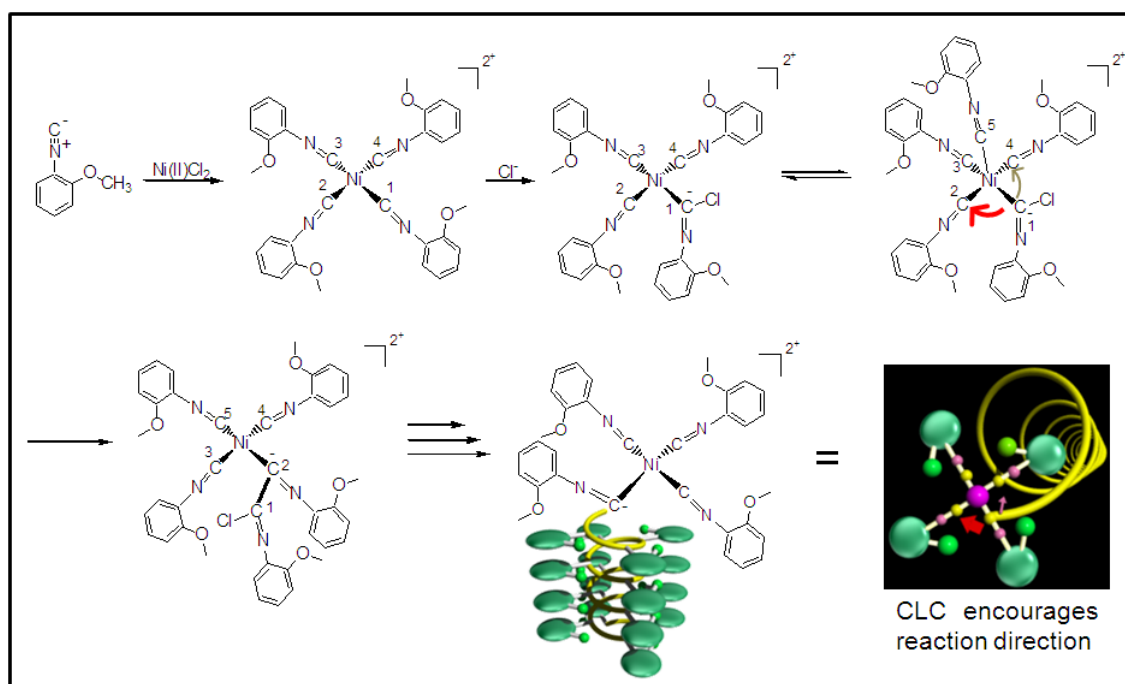
**Fig. 6.** CD (upper) and absorption (below) spectra were measured in (a) tetrahydrofuran (THF), (b) chloroform, (c) *N,N*-dimethylformamide (DMF) and (d) dimethylsulfoxide (DMSO) with poly-**3r** (0.02–0.03 mg/mL).



**Fig. 7.** Change of CD intensity (456 nm) of poly-**3r** in DMSO (0.02 mg/mL) with multiple thermal cycles of heating to 110 °C and cooling to 20 °C.



**Fig. 8.** CD (upper) and absorption (below) spectra for poly-**3ri** in chloroform solution (0.02 mg/mL).



**Fig. 9.** A proposed mechanism for the polymerization of 2-methoxyphenyl isocyanide in CLC phase.

*Supporting Information for:*

## Catalysis Direction Selective Asymmetric Polymerization in Chiral Liquid Crystal Medium

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### Monomer Synthesis

*General procedure for preparation of N-arylisocyanides (GP1).*

Arylformanilides (1 g, 6.6 mmol) and diisopropylamine (2.5 mL, 17.8 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) and cooled to -2 °C using an ice-salt bath. POCl<sub>3</sub> (0.68 mL, 7.3 mmol) was slowly added dropwise and stirring was continued at 0 °C for another 90 min. Then, a 10% aq Na<sub>2</sub>CO<sub>3</sub> solution was added and the two phase mixture was stirred for another 30 min at rt. The aqueous layer was separated and extracted with dichloromethane and dried over MgSO<sub>4</sub>. The solvent was evaporated, and the residue was purified by silica gel column chromatography to afford the target isocyanides.

*2-Methoxyphenyl isocyanide (3).*

Yield: 0.47 g (3.5 mmol, yield = 53%) as liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.37-7.33 (m, 2H), 6.97-6.91 (m, 2 H), 3.93 (s, 3H).

*3-Methoxyphenyl isocyanide (4).*

Yield: 0.38 g (2.9 mmol, yield = 42%) as liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.30-7.28 (d, 1H), 6.98-6.86 (m, 3H), 3.82 (s, 3H).

*2,6-Dimethoxyphenyl isocyanide (6).*

The procedure 2 was followed using 2,6-dimethoxyphenyl formamide (0.40 g, 2.2 mmol),

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DIPA (0.82 mL, 5.9 mmol), POCl<sub>3</sub> (0.22 mL, 2.4 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL). Yield: 0.24 g (1.5 mmol, 68%) as liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.27 (t, 1H), 6.56 (d, 2H), 3.91 (s, 6H).

*General procedure for preparation of “convertible” N-arylisocyanides (GP2).*

The isocyanides were prepared according to the previously reported procedure.<sup>(1)</sup> Benzoxazole (0.90 g, 7.56 mmol) was dissolved to THF and the mixture was cooled to -78 °C. Then *n*-BuLi (1.6 M solution in hexanes, 5.4 mL, 8.64 mmol) was slowly added dropwise and stirring was continued at -78 °C for 90 min. The acyl chloride (acid chloride) (7.94 mmol) was added dropwise to the solution, while the solution was stirred at rt for 120 min. The reaction mixture was poured onto a mixture of ether (100 mL) and saturated aqueous NaHCO<sub>3</sub> (50 mL). The organic layer was washed with water and dried over by MgSO<sub>4</sub>. The solvent was evaporated, and the residue was purified by silica gel column chromatography to afford the target isocyanides.

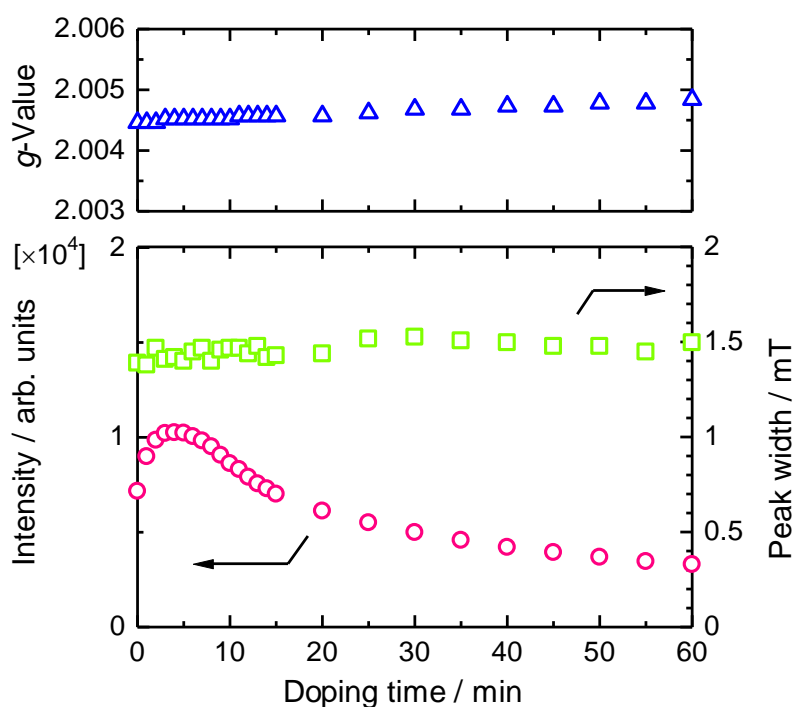
*2-Isocyanophenyl acetate (2).*

Yield: 0.78 g (4.84 mmol, 64%) as liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.45-7.41 (m, 2H), 7.29-7.21 (m, 2H), 2.40 (s, 3H).

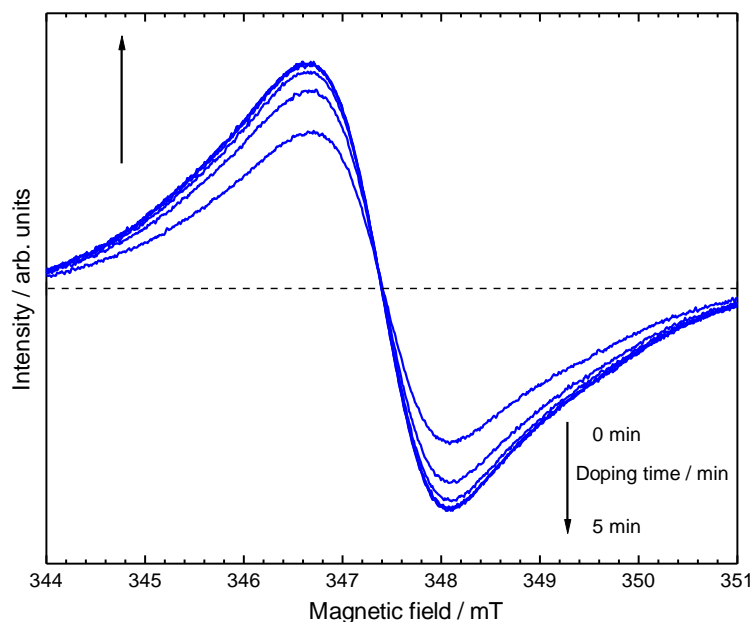
*2-Isocyanophenyl isobutyrate (5).*

Yield: 0.23 g (1.19 mmol, 16%) as liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.45-7.40 (m, 2H), 7.28-7.19 (m, 2H), 2.91 (sept, 1H), 1.39 (d, 6H).

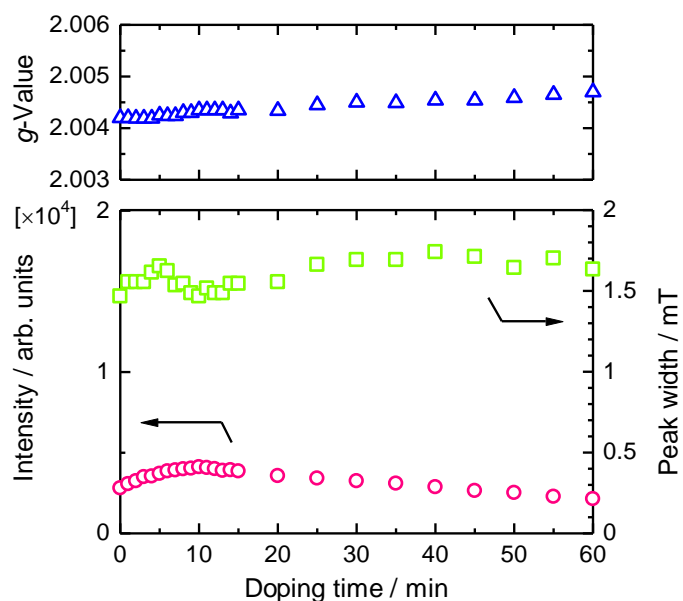




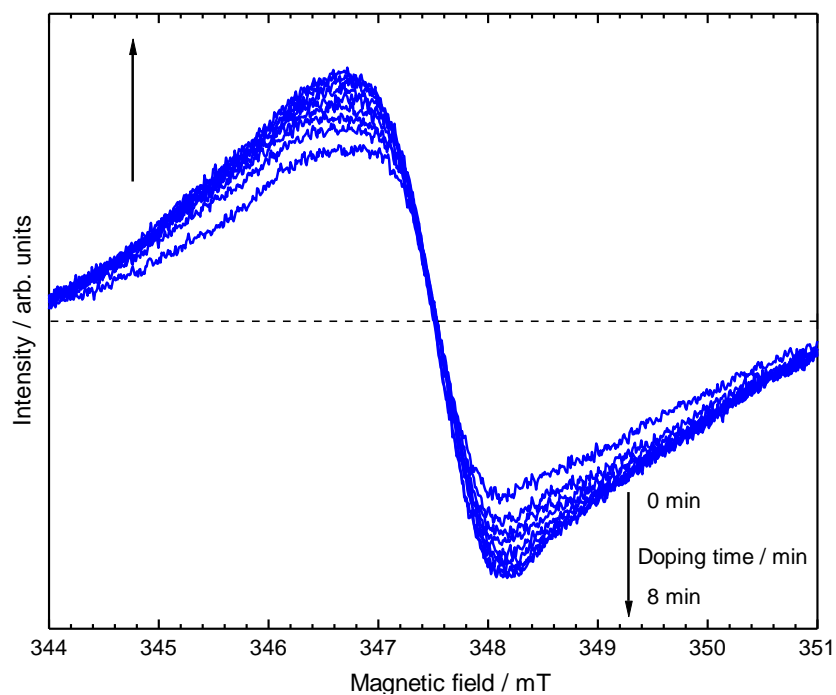
**Fig. S1.** ESR intensity,  $g$ -value, and peak width ( $\Delta H_{pp}$ ) of the ESR signal for poly-**3r** during *in-situ* vapor-phase iodine doping.



**Fig. S2.** *In-situ* ESR spectra of poly-**3r** during vapor phase iodine doping for 0–5 min.



**Fig. S3.** ESR intensity,  $g$ -value, and peak width ( $\Delta H_{pp}$ ) of the ESR signal for poly-**3n** during *in-situ* vapor-phase iodine doping.

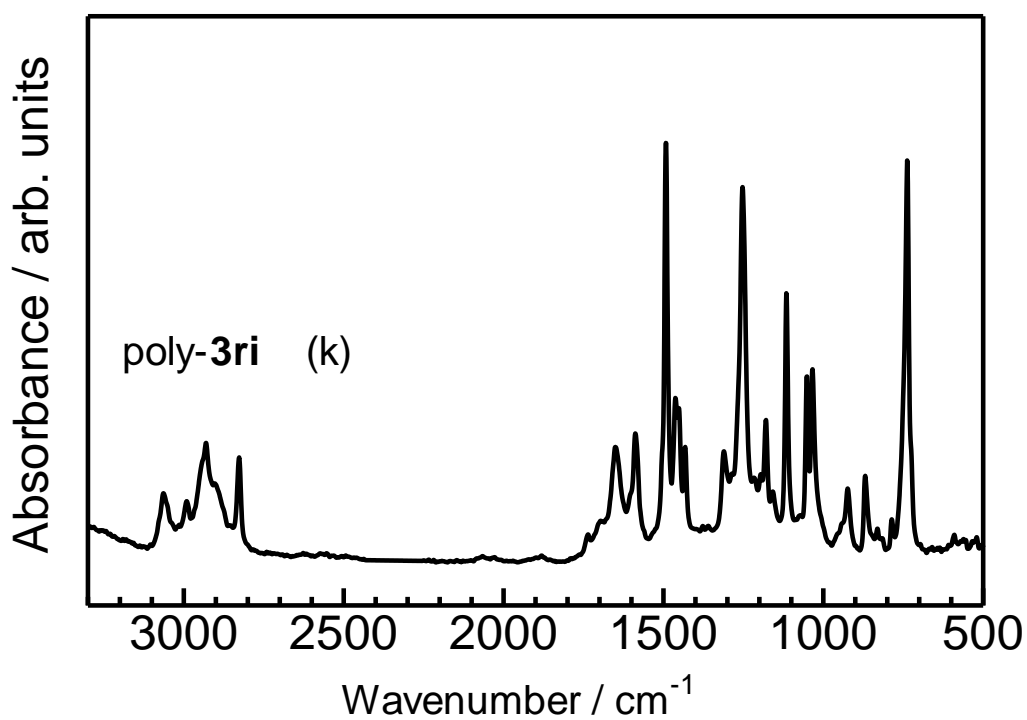


**Fig. S4.** *In-situ* ESR spectra of poly-**3n** during vapor phase iodine doping for 0–8 min.

**Table S1.** Polymerization of monomer **3** with annealing

Monomer	Polymer	Polymerization condition			$M_n^a$	$M_w^a$	$M_w/M_n^a$	Yield (%) <sup>b</sup>
		Solvent	Temp	Phase				
<b>3</b>	poly- <b>3ri</b>	( <i>R</i> )-CLC	100 °C → 140 °C	CLC → isotropic	3,000	3,500	1.2	45

<sup>a</sup> Determined by gel permeation chromatography (GPC) and relative to polystyrene standards (eluent: THF). <sup>b</sup> Isolated yield of high molecular weight fraction.



**Fig. S5.** IR absorption spectrum of poly-**3ri** (k).

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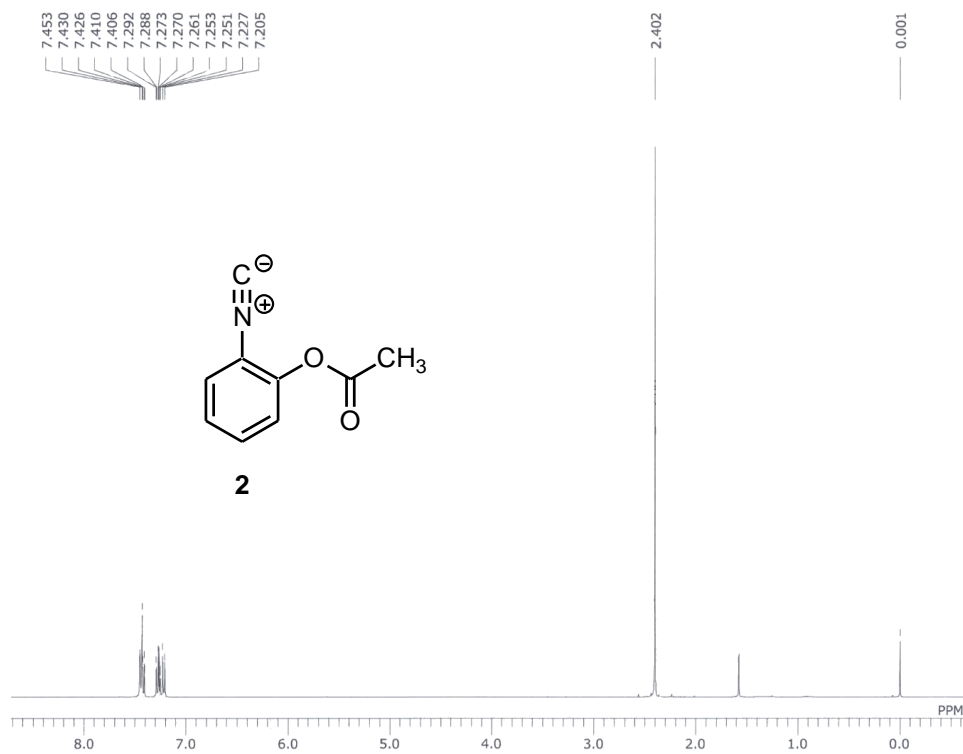


Fig. S6. <sup>1</sup>H NMR spectrum (400 MHz) of 2.

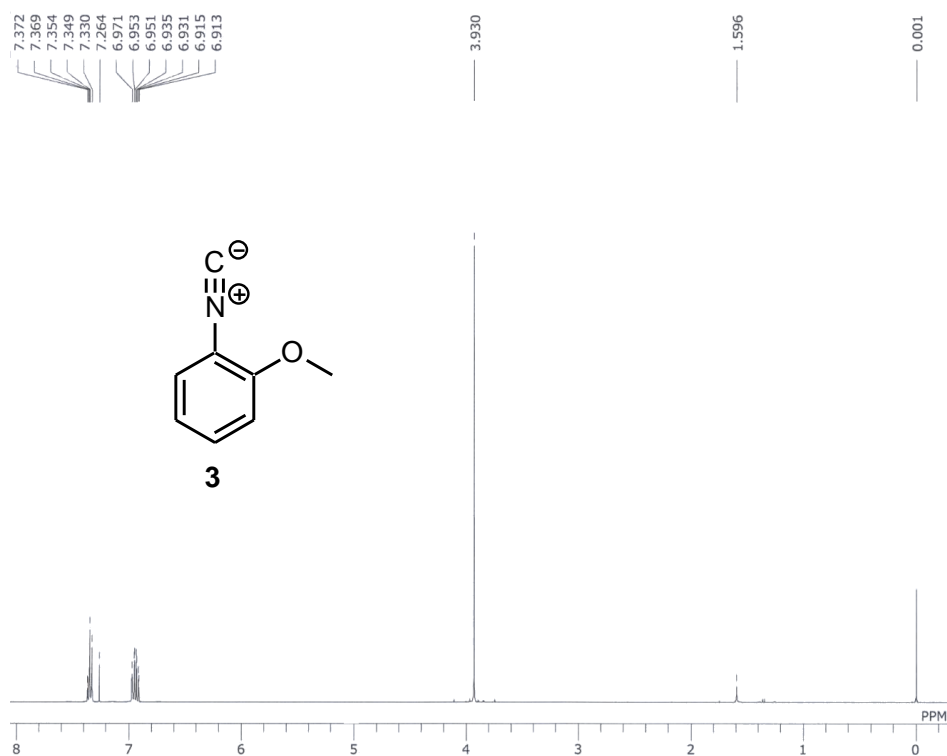


Fig. S7. <sup>1</sup>H NMR spectrum (400 MHz) of 3.

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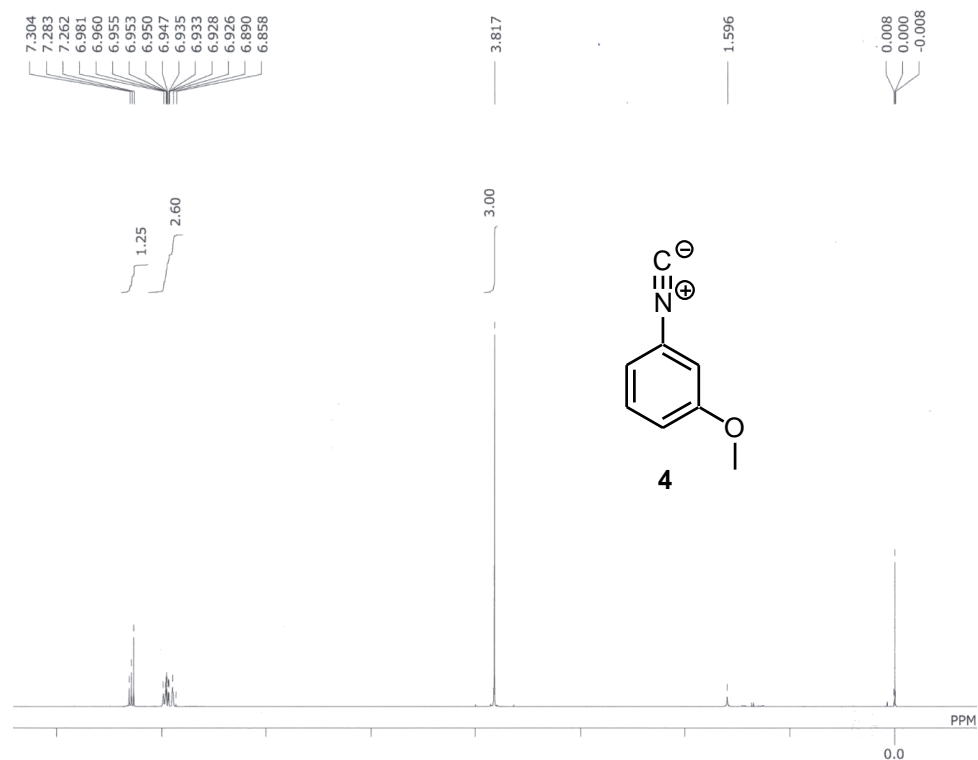


Fig. S8. <sup>1</sup>H NMR spectrum (400 MHz) of 4.

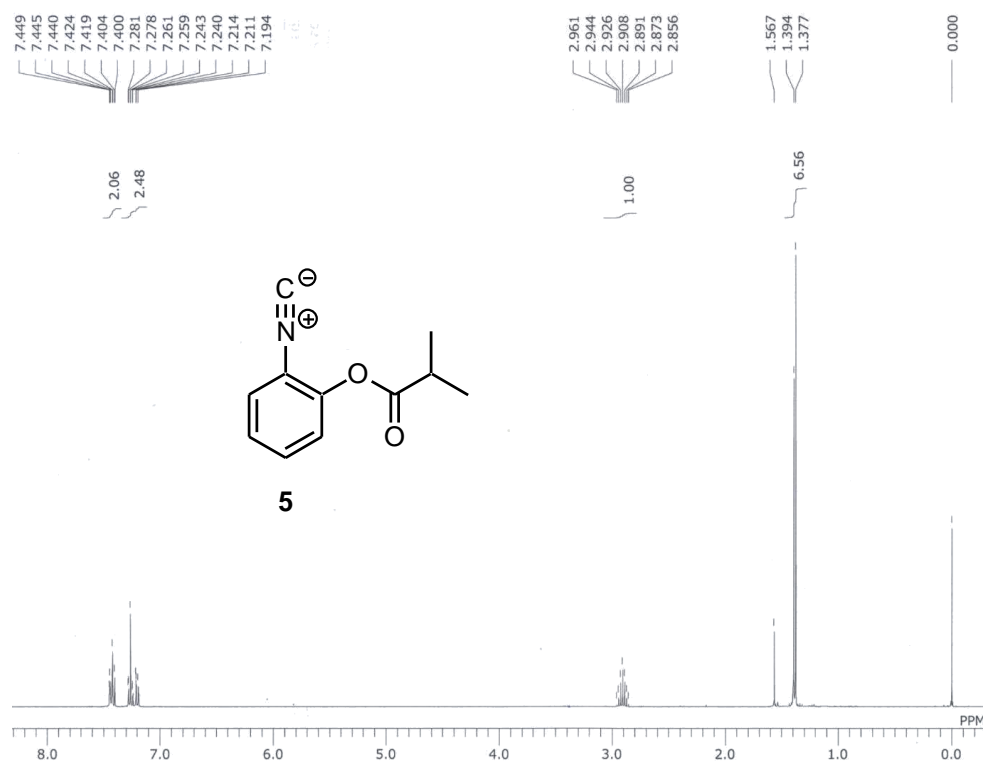
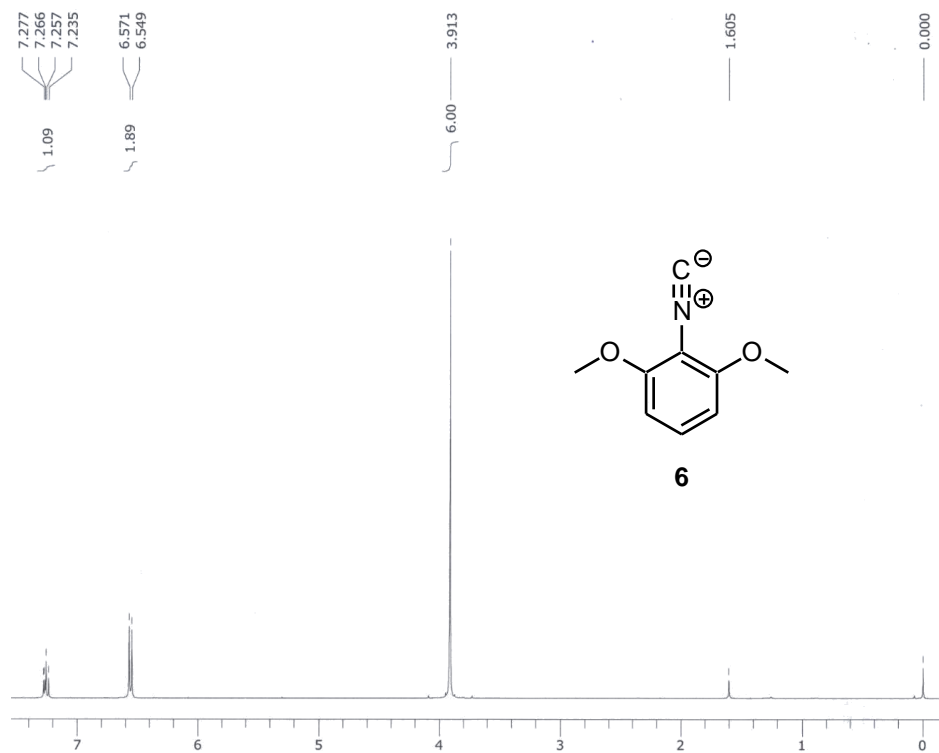


Fig. S9. <sup>1</sup>H NMR spectrum (400 MHz) of 5.

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**Fig. S10.**  $^1\text{H}$  NMR spectrum (400 MHz) of **6**.

### Reference

(1) M. C. Pirrung and S. Ghorai, *J. Am. Chem. Soc.* 2006; 128: 11772-11773.