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Structural chirality of cholesteric liquid crystal produces atropisomerism: Chiroptical polyisocyanides from achiral monomer in cholesteric liquid crystal matrix

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ABSTRACT

1-Naphthyl isocyanide was polymerized with Ni(II) catalyst in a cholesteric matrix at the liquid crystal (LC) temperature range. The resultant polymers showed optical activity. In this reaction, the structural chirality of cholesteric LC effectively functions to impart one-handed helicity on the corresponding polymers as an optically active atropisomer.

1. Introduction

Synthetic chiral polymers [1], such as polyaniline bearing camphor sulfonic acid [2], polysilanes [3], and polythiophene [4] with chiroptical activity, have been synthesized for the development of novel functions and biomimetic technology. Induction of optical activity for a polymer in solution by the external environment has been demonstrated, such as chirality transfer from a chiroptical solvent to poly(*n*-hexyl isocyanate) of an optically inactive polymer [5].

Polyisocyanides have been investigated in the chiral polymer research; due to their unique main chain helical structure [6]. Polyisocyanides form a stable 4_1 helical conformations in a solution, and the introduction of an appropriate chiral side chain maintains the one-handed helical structure. Atropisomerism in polymers has been demonstrated for polyisocyanides [7]. Chiroptically active polyisocyanides having a side chain, such as polyisocyanides with an alanine-based substituent [8], polyisocyanopeptides [9], and poly(zwitterionic isocyanides) with birefringence [10], and liquid crystalline polyisocyanide [11], have been studied. Helical sense-selective polymerization initiated by aryl–rhodium complexes has been developed [12], and the synthesis and doping effect of tetrathiafulvalene-substituted polyisocyanide has been performed [13]. The helical structure has been directly observed using atomic force microscopy (AFM) for polyisocyanides prepared by helical sense-selective living block copolymerization, which provided evidence that polyisocyanides clearly form a helical structure [14]. Polymerizations of chiral isocyanides as monomers in isotropic solvents were performed. This produces right- and left-handed helical poly isocyanides whose helical sense can be controlled by the polymerization solvents and temperature. The resultant polymers show lyotropic liquid crystallinity [15].

Liquid crystal (LC) science and technology have been developed for materials science such as synthesis of new functional LC materials [16], and preparation of uniaxial alignment of the nanotubes by using lyotropic LC [17]. Chiral LC, especially cholesteric LC shows characteristic properties. The individual molecules of cholesteric LCs aggregate in a three-dimensional (3-D) one-handed helical structure for the formation of structural chirality.

Cholesteric LCs can play a role of chiral matrix for chemical reactions under appropriate conditions. A cholesteric LC matrix was employed to obtain optically active polythiophene derivatives from optically inactive monomers [4]. The polythiophenes displayed chiroptical activity based on chiral aggregation derived from a cholesteric LC-like order. Furthermore, electrochemical driven control of chiroptical activity was developed [18], and charge career (polarons) in helical form has been proposed for polymers prepared in cholesteric LC [19].

In this study, optically active poly(1-naphtyl isocyanide) is synthesized in a cholesteric LC matrix with the aid of a $NiCl_2$

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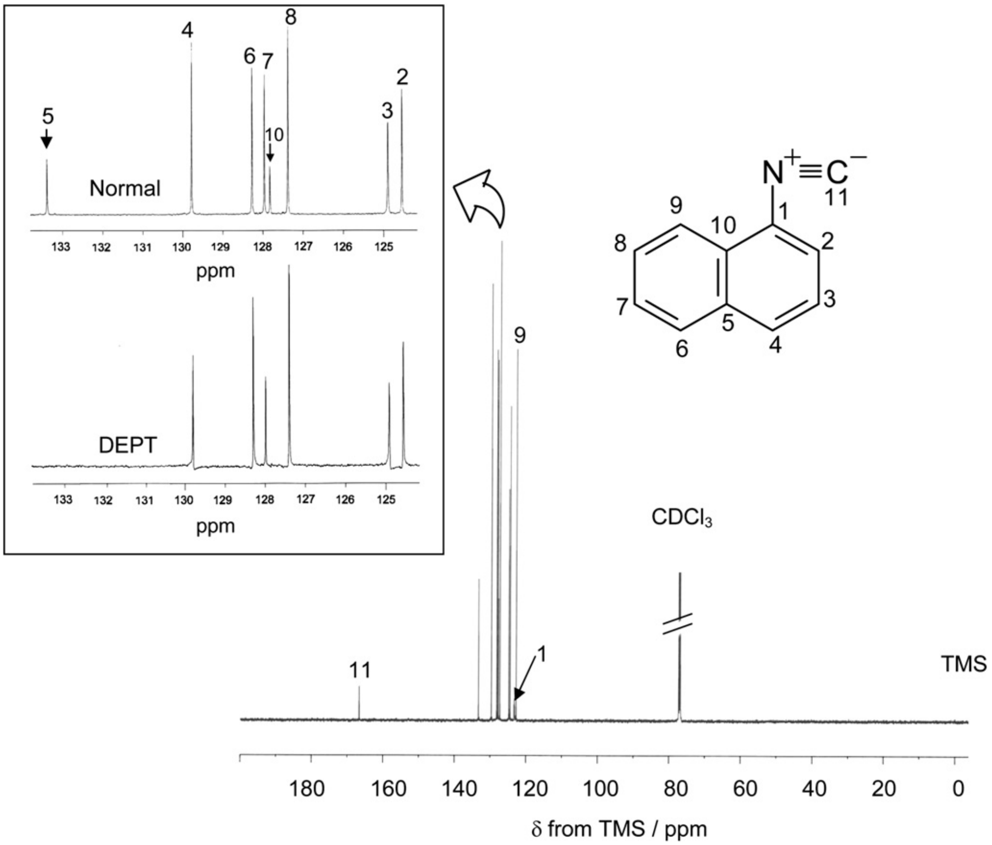

Fig. 1. ^{13}C NMR of 1-naphtyl isocyanide. Inset shows high magnetic region of distortion enhance polarized transfer (DEPT) and normal ^{13}C NMR spectra. Arrows show signals of carbons having no protons revealed with DEPT.

catalyst. After removal of the cholesteric matrix, the resultant was dried in vacuum to give polymer in powder. The polymers thus obtained exhibit the Cotton effect in achiral solution at the corresponding wavelength of the π−π* transition of the side chain and the n−π* transition of the main chain, which indicates that both the side chain and the main chain form stable one-handed helical structures. Thus, synthesis of the one-handed helicoidal polymer as an optically active atropisomer was performed with 3-D structural chiral matrix of cholesteric liquid crystal. The helicity is maintained by inter-lock function between side chains through π-stacking.

The chiroptical activity of the polymers in this study may originate from atropisomerism for the polyisocyanides produced by the cholesteric matrix. This can be referred to as a chiral field effective reaction in a cholesteric matrix.

2. Experimental

2.1. Syntheis of cholesteric liquid crystal medium

Cholesteric (Ch*) LC compounds having a three ring system with terminal alkyl groups that have (*R*) and (*S*) configurations (4-ethoxy-benzoic acid 4′-[(*R*)-1-methyl-heptyloxy]biphenyl-4-yl ester and 4-ethoxy-benzoic acid 4′-[(*S*)-1-methyl-heptyloxy] biphenyl-4-yl ester), abbreviated as (*R*)-Ch*LC and (*S*)-Ch*LC, were prepared as cholesteric matrices using a previously reported method [20]

2.2. Monomer synthesis

Basically synthesis of the monomer was performed according to the method reported in the literature [21]. A solution of *tert*-butanol 24 mL, $(CH_3)_3COK$ (1.8 g, 16 mmol) in three necked round bottom flask was stirred for 2 days at 45 °C under argon flow. This solution was added to another solution of 1-naphthylformamide (1 g, 8.2 mmol) in *tert*-butanol (4 mL) very slowly. After 24 h, $POCl_3$ (0.54 g, 35 mmol) was added to the mixture and stirred for 40 min at 10–20 °C. Further, the reaction mixture was stirred for 1 h at room temperature. The mixture was poured into a large volume of aqueous $NaHCO_3$ (10 wt%, 50 mL) solution, the organic layer was extracted with ether. The ether solution was dried with $MgSO_4$. After filtration, the crude product was dissolved in *n*-hexane (20 mL) and cooled. The precipitation was removed by

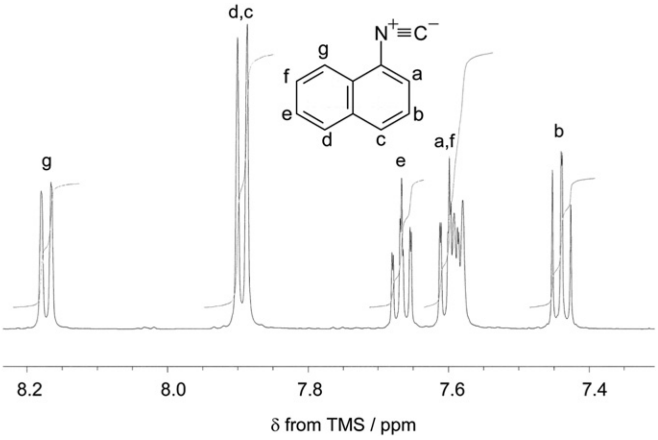

Fig. 2. ^{1}H NMR of 1-naphtyl isocyanide.