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Synthesis and properties of mono-substituted liquid crystalline polyacetylene derivatives—doping, magnetic orientation, and photo-isomerization

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Abstract

Mono-substituted acetylene monomers with a liquid crystalline (LC) group are polymerized using rhodium, iron or molybdenum complex catalysts. LC polyacetylene derivatives with number-averaged molecular weights of 4000–330000 were obtained in 5–92% yield. The LC behavior is examined by X-ray diffraction, differential scanning calorimetry, and polarizing optical microscopy. The polymers prepared using rhodium or iron catalyst are confirmed to assume a *cis* form and to undergo an irreversible isomerization to the *trans* form upon heating. Photo-responsive polyacetylene derivatives are successfully synthesized through the introduction of an azobenzene moiety as a mesogenic core into the side-chain, and these forms exhibit a reversible photochemical *cis*-to-*trans* isomerization of the azobenzene moiety.

Keywords: Liquid crystals; Polyacetylene; Polymer; Photo-induced isomerization; Magnetic orientation

1. Introduction

Conjugated polymers exhibit electrical transport, nonlinear optical (NLO), and organic magnetic phenomena. Iodine-doped polyacetylene in particular, regarded as a representative organic conductor, has electrical conductivity comparable to metals. This high conductivity has also been achieved in macroscopically aligned polyacetylene films. In 1987, a directly aligned polyacetylene film using liquid crystal (LC) as a solvent under a magnetic field was synthesized [1]. It has been confirmed through scanning electron microscopy that the high conductivity of this highly oriented polyacetylene is due to the strongly aligned fibril morphology. LC ordering is thus considered to provide an effective and useful anisotropic environment for polymer synthesis.

LC is unique in that it exhibits both crystal-like birefringence and fluid behavior. Conjugated polymers with LC side-chains are intriguing classes of polymer [2]. In the side-chain LC conjugated polymer, the side-chain array in the LC state induces spontaneous orientation of the polymer, which may be attended to improve the main-chain coplanarity. Furthermore, through the application of an external force, such as shear stress or an electric/magnetic field, the orientation can be controlled on a macroscopic scale.

In the present study, polyacetylenes bearing various types of functional LC are synthesized, and the liquid crystallinity, doping effects, magnetic orientation, and photo-induced isomerization are examined as an exploration of the potential of liquid crystalline conjugated polymers.

2. Synthesis

2.1. Monomer synthesis

The syntheses of 5-[4-(*trans*-4′-*n*-alkylcyclohexyl)phenoxy]-1-pentyne, 1-[4-(*trans*-4′-pentylcyclohexyl)phenoxy]-6-bromohexane, and 5-(4-pentyl-4′-biphenoxy)-1-pentyne were carried out by the method described in the literature [3,4(e)]. Here, the three monomers are denoted PCHR03A, PCH506Br, and BP503A, respectively, where P denotes phenyl, CH denotes

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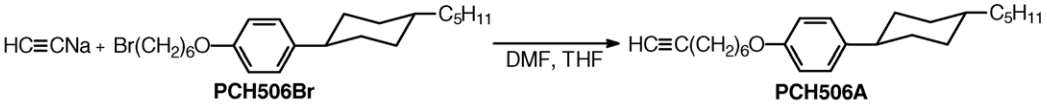
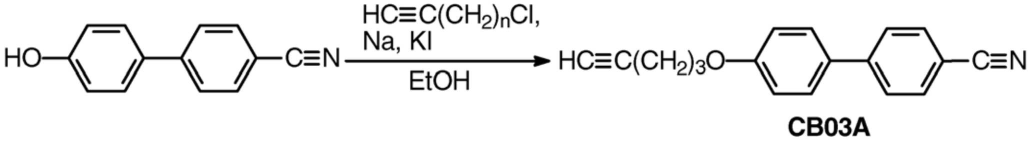
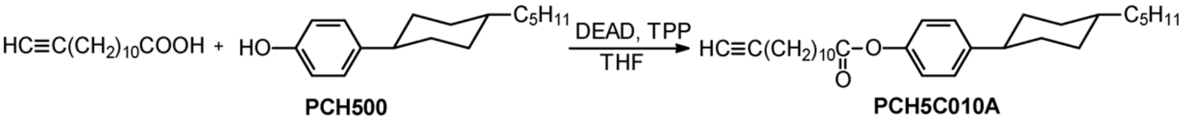


Scheme 1.



Scheme 2.



Scheme 3.

cyclohexyl, *R* is the carbon number of terminal alkyl groups, 0 is ether oxygen, 3 (6) is the carbon number of flexible alkyl spacers, A denotes acetylene, Br denotes bromine connected to alkyl spacer, and BP denotes biphenyl.

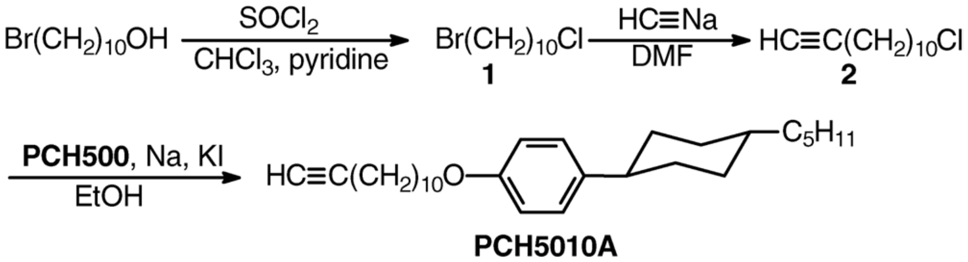
The coupling reaction between sodium acetylide and PCH506Br in *N,N′*-dimethylformamide (DMF) afforded PCH506A in 10% yield (Scheme 1).

CB03A was prepared via Williamson reaction by etherification between 4′-hydroxy-biphenyl-4-carbonitrile and 5-chloro-1-pentyne in the presence of potassium iodide as a catalyst (Scheme 2).

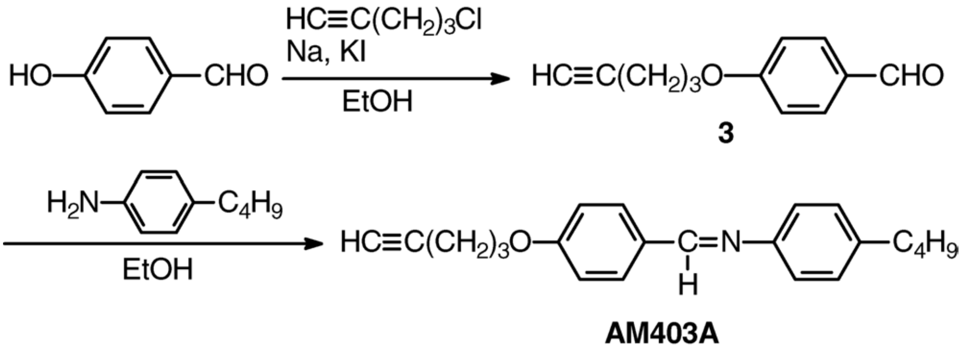
The synthetic route to PCH5C010A (5-carbon terminal alkyl group, C0: ester group, 10-carbon flexible alkyl spacer) is described in Scheme 3. PCH5C010A was prepared via Mitsunobu reaction by esterification between tridec-12-ynoic acid and 4-(*trans*-4′-*n*-pentylcyclohexyl)phenol (PCH500) using diethylazodicarboxylate (DEAD) and triphenyl phosphine (TPP).

10-Bromodecan-1-ol was converted to 10-bromodecan-1-chloride using $SOCl_2$ and then coupled with sodium acetylide to afford **2**. Subsequently, compound **2** was coupled with PCH500 to afford PCH5010A with a long alkyl spacer (Scheme 4).

An acetylene monomer with azomethine (AM) LC group was prepared via the synthetic route described in Scheme 5. 4-Hydroxybenzaldehyde and 5-chloro-1-pentyne were coupled using sodium in the presence of potassium iodide by Williamson



Scheme 4.



Scheme 5.