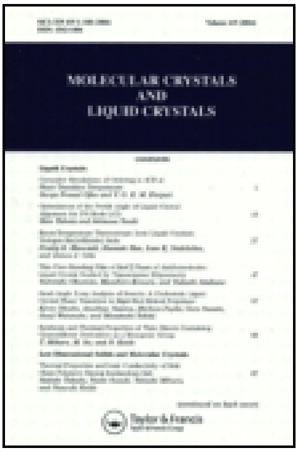

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Synthesis of Liquid Crystalline Polyacetylene Derivatives

Hideki Shirakawa [a], Yasuo Kadokura [a], Hiromasa Goto [a], Se-Young Oh [a], Kazuo Akagi [a] & Kotaro Araya [b]

[a] Institute of Materials Science, University of Tsukuba, Ibaraki, 305, JAPAN

[b] Advanced Research Laboratory, Hitachi Ltd., Saitama, 350-03, JAPAN

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SYNTHESIS OF LIQUID CRYSTALLINE POLYACETYLENE DERIVATIVES

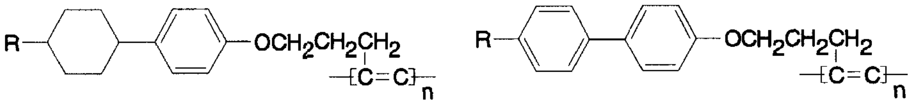
HIDEKI SHIRAKAWA, YASUO KADOKURA, HIROMASA GOTO,
SE–YOUNG OH, KAZUO AKAGI,
Institute of Materials Science, University of Tsukuba, Ibaraki 305 JAPAN
KOTARO ARAYA,
Advanced Research Laboratory, Hitachi Ltd. Saitama 350–03 JAPAN

Abstract Mono–substituted acetylenes with liquid crystalline group consisting of phenylcyclohexyl and biphenyl moieties as mesogenic cores have been synthesized and polymerized using Ziegler–Natta and metathesis catalysts. Measurements of DSC and polarized microscopy showed that the polymers have smectic liquid crystal phases, while the monomer with phenylcyclohexyl moiety linked with octyl terminal group has nematic phase.

INTRODUCTION

The application of external perturbation such as electric or magnetic force field into the side–chain liquid crystalline conjugated polymers is expected to enhance anisotropy of electrical and magnetic properties by virtue of alignment of main chain in accompany with the orientation of the liquid crystalline side chain. In this sense, the poly(mono–substituted acetylene)s with liquid crystalline group in the side chain should become a candidate for the advanced functional conducting polymers. Recently we synthesized a series of mono–substituted polyacetylene derivatives with phenylalkyl groups and liquid crystalline groups consisting of phenylcyclohexy mesogen in the side chain.[1–3]

Here we present syntheses and polymerization of two kinds of mono–substituted acetylene monomers, and characterization of their polymers. The liquid crystalline substituent of the monomer is composed of phenylcyclohexyl (PCH) moiety as a mesogen core, a methylene chain linked with ether linkage, $-(CH_2)_3O-$, as a spacer, and an alkyl chain, *n*–octyl, as a terminal group. This monomer is abbreviated as PCH803A, where A, 8, and 03 stand for the terminal acetylene, the terminal alkyl group, and the spacer, respectively. Another kind of the substituent consists of a biphenyl (BP) mesogen core, methylene chain linked with oxygen as a spacer, and *n*–pentyl group as a terminal moiety. This type of monomer is abbreviated as BP503A. These monomers were polymerized using Ziegler–Natta and metathesis catalysts. Similarly, the corresponding polymers are abbreviated as PPCH803A and PBP503A, as shown in Scheme 1.



R = *n*-octyl : PPCH803A R = *n*-pentyl : PBP503A

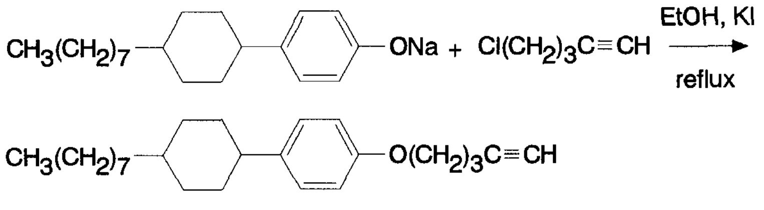
Scheme 1

The present monomers and polymers were characterized by means of IR, UV-Visible, ^{1}H- and ^{13}C-NMR, elemental analyses, as well as differential scanning calorimetry (DSC) and polarized microscopy. The molecular weights of the polymers were evaluated by GPC using polystyrene standards, and electrical conductivities upon iodine doped polymers were measured by two-probe method.

EXPERIMENTAL

1. Synthesis of monomers

PCH803A was synthesized as shown in Scheme 2 through a reaction of p-(*trans*-4'-octylcyclohexyl)phenol and 5-chloro-1-pentyne in sodium ethoxide by using potassium iodide as a catalyst.

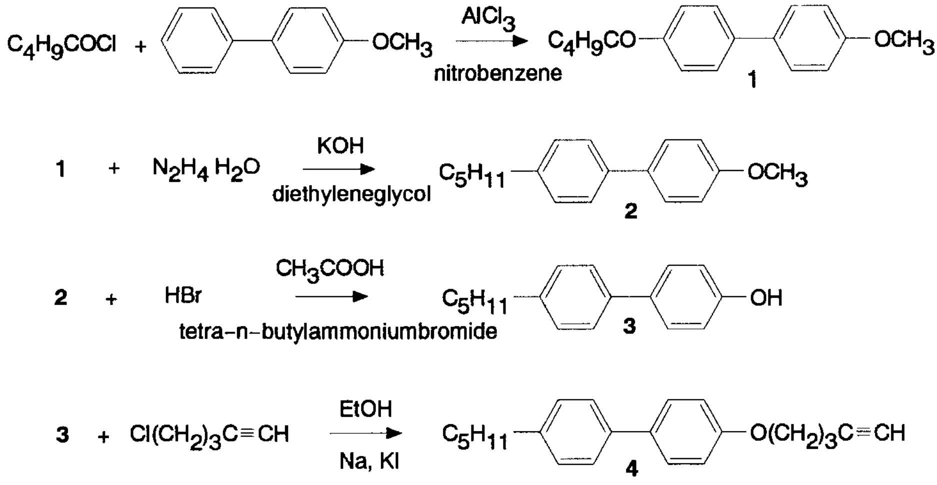


Scheme 2

The four step synthesis of BP503A is shown in Scheme 3. First, 4-methoxy-4'-pentanoylbiphenyl (**1**) was synthesized through Friedel-Crafts reaction between 4-methoxybiphenyl and pentanoylchloride. The carbonyl moiety of **1** was reduced into methylene group by hydrazine and potassium hydroxide in diethyleneglycol to yield 4-methoxy-4'-pentylbiphenyl (**2**). The methoxy group in 2 was changed into hydroxy one using hydrogen bromide in acetic acid. The etherification of **3** was carried out through coupling reaction with 5-chloro-1-pentyne in sodium ethoxide using potassium iodide as a catalyst, yielding 5-*p*-pentylbiphenoxy-1-pentyne (BP503A) (**4**).

2. Polymerization of the monomers

Polymerizations of PCH803A and BP503A were carried out using Ziegler-Natta catalyst ($Fe(acac)_3$–$AlEt_3$) and metathesis catalyst ($MoCl_5$–Ph_4Sn) in toluene for 21 h at room temperature. The reaction was terminated by pouring the reaction mixture into a large amount of methanol. The polymers were filtered off and washed with methanol and then dried under vacuum.



Scheme 3

RESULTS AND DISCUSSION

The polymerization yield and molecular weight of the polymers evaluated from GPC measurement are summarized in Table I. $MoCl_5$–Ph_4Sn catalyst gave higher yields than the $Fe(acac)_3$–$AlEt_3$ catalyst.

Table 1 Polymerization of PCH803A and BP503A by $Fe(acac)_3$–$AlEt_3$ and $MoCl_5$–Ph_4Sn

Monomer	Catalyst	Yield (%)	Mn	Mw	Mw/Mn
PCH803A	$Fe(acac)_3$–$AlEt_3$	67	5.2×10^5	2.4×10^6	5.0
	$MoCl_5$–Ph_4Sn	73	1.2×10^4	2.7×10^4	2.3
PBP503A	$Fe(acac)_3$–$AlEt_3$	65	3.5×10^3	1.0×10^4	2.9
	$MoCl_5$–Ph_4Sn	85	7.3×10^3	6.8×10^4	9.1

Polymerized in toluene for 21 h at room temperature.
[Monomer] = 3 mmol, $[Fe(acac)_3] = 0.01$ mol/l, $[AlEt_3]/[Fe(acac)_3] = 6$,
$[MoCl_5] = 0.01$ mol/l, $[Ph_4Sn]/[MoCl_5] = 0.5$.

The high molecular weight more than 10^5 in Mn of the PPCH803A using the Fe–based catalyst is worth to be emphasized. Note that although the PBP503A prepared with the Fe–based catalyst was insoluble in THF and benzene in the range of room temperature to 90 °C, it became soluble into cumene by heating up to 120 °C for 30 min. Thus dissolved polymer has low viscosity and relatively small molecular weight of 3000 – 4000 in Mn. This may be due to the degradation during the heating process.

The monomer of PCH803A and the intermediate compounds of 4–methoxy–4'–pentanoylbiphenyl (**1**), and 4–methoxy–4'–pentylbiphenyl (**2**), were found to show mesophase from DSC measurement and polarized microscope observation. The liquid crystalline phases of these compounds were observed only in the cooling process but not in the heating one, indicating monotropic liquid crystal. The phase transition temperature observed for the polymers are shown in Table 2.

Table 2. Phase transition temperatures of PPCH803A and PBP503A polymers

Polymer	Catalyst	first cooling			second heating		
		C	S_A	I	C	S_A	I
PPCH803A	$Fe(acac)_3$–$AlEt_3$	81	146		83	136	
	$MoCl_5$–Ph_4Sn	86	170		90	166	
PBP503A	$Fe(acac)_3$–$AlEt_3$	128	185		129	180	
	$MoCl_5$–Ph_4Sn	130	210		135	200	

C = crystalline, S_A = smectic A, and I = isotropic. (°C)

The PPCH803A prepared by the Fe–based catalyst exhibited a large exothermic peak due to the *cis–trans* isomerization at 100 – 176 °C in the first heating. The endothermic peak around 180 °C was hidden by this isomerization peak. In the first cooling, the peak of isotropic to liquid crystal phase transition was observed at 146 °C, and that of liquid crystal to solid phase at 81 °C. In the second heating, the liquid crystal phase was observed in temperature range of 83 – 136 °C.

The PPCH803A polymer prepared by the Mo–based catalyst showed a broad exothermic peak in the range of 150 – 190 °C in the first heating. The polarized microscope indicated a transition from liquid crystal to isotropic phase in the temperature range. In the first cooling, transition peaks from isotropic to liquid crystalline phase and from liquid crystalline to solid phase were observed at 170 and 86 °C, respectively. In the second heating, the mesophase was observed in the range of 90 – 160 °C.

Both polymers, PBP503As prepared by the Fe– and Mo–based catalysts showed similar DSC curves. In the first heating, the *cis–trans* isomerization peak was observed at 140 °C, and the broad endothermic peak due to the melting was observed at higher temperature. The temperature range of the liquid crystalline phase of PBP503A by the Fe–based catalyst were 128 – 185 °C and 129 – 180 °C in the first cooling and the second heating, respectively. While, those of PBP503A prepared by the Mo–based catalyst were 130 – 210 °C and 135 – 200 °C in the first cooling and the second heating processes, respectively.

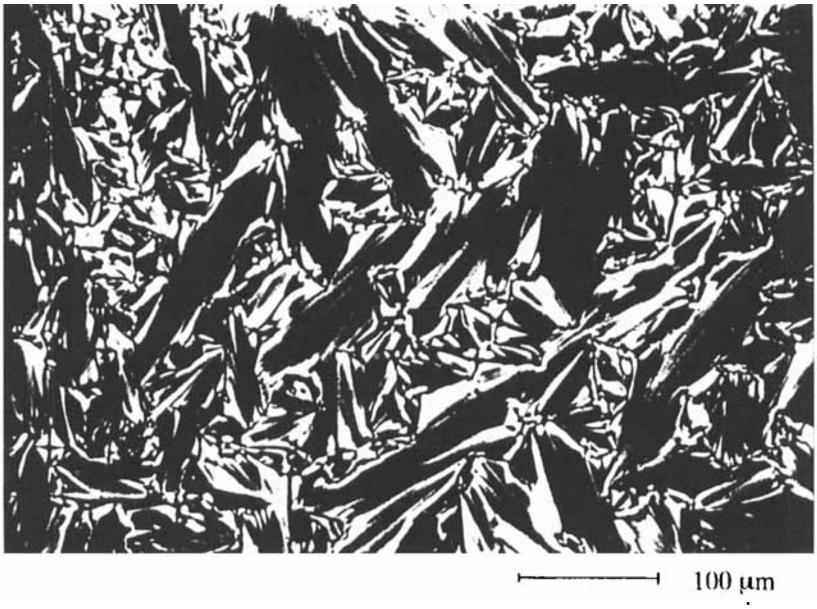


Figure 1 The fun-shaped texture of the S_A phase at 149 °C on the first cooling scan displayed by PPCH803A prepared by the Mo-based catalyst.

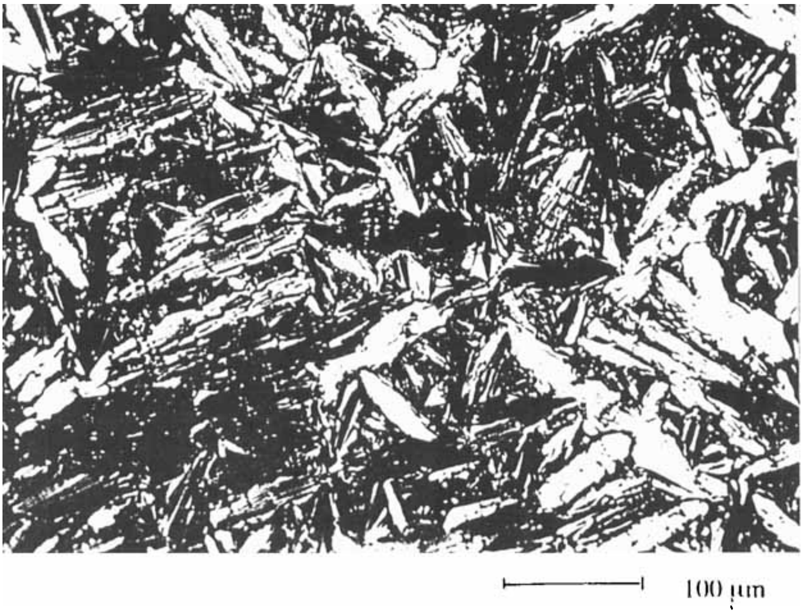


Figure 2 The fun-shaped and bâtonets textures of the S_A phase at 120 °C on the first cooling scan displayed by PBP503A prepared by the Mo-based catalyst.

In contrast to the case of the PCH803A monomer and intermediate compounds, the mesophase in the PPCH803A and PBP503A polymers were observed in both the heating and cooling processes, indicating an enantiotropic liquid crystal of the polymers, irrespective of the catalyst species used in the present polymerization. The polarized microscope of the polymers in the mesophase showed a fan-shaped or batonet texture that is characteristic to smectic A phase. Typical fan-shaped texture of the PPCH803A and the PBP503A prepared by the Mo-based catalyst is shown in Figure 1 and 2, respectively.

The domain size of liquid crystal phase was found to increase with lengthening of terminal alkyl chain length in the side-chain of the PCH polymer. Meanwhile, the domain size in the PBP503A polymer prepared by the Mo-based catalyst was larger that by the Fe-based catalyst. This is consistent with the experimental fact that the former is thermally more stable than the latter.

Lastly it is of keen interest to emphasize that the PCH803A monomer shows a nematic liquid crystal, while the corresponding polymer shows a smectic one which has a higher order than the nematic structure. This can be rationalized with so-called polymerization effect, i.e., a higher order in molecular arrangement of liquid crystal phase was generated by the polymerization. Electrical conductivity of the polymers was 10^{-3} - 10^{-2} S/cm upon iodine doping to the cast films. The alignment of the polymer chain accompanied with the side-chain orientation using an external perturbation would enhance further the electrical conductivity. This sort of study is now under way and will be reported in the near future.

CONCLUSION

We synthesized two kinds of liquid crystalline polyacetylene derivatives by using both Fe-based Ziegler-Natta catalyst and Mo-based metathesis catalyst. The polymers showed not only enantiotropic smectic A phase, by virtue of side-chain composed of phenylcyclohexyl or biphenyl mesogenic moiety, but also electrical conductivity upon iodine doping.

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