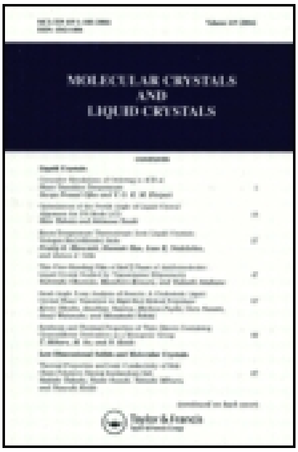


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electrically Conducting Liquid Crystalline Polymers, Mono-Substituted Polyacetylene Derivatives

Kazuo Akagi [a] , Hiromasa Goto [a] , Kiyoshi Iino [a] , Hideki Shirakawa [a] & Junichi Isoya [b]

[a] Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki, Japan

[b] University of Library and Information Science, Tsukuba, Ibaraki, Japan

Version of record first published: 24 Sep 2006.

To cite this article: Kazuo Akagi , Hiromasa Goto , Kiyoshi Iino , Hideki Shirakawa & Junichi Isoya (1995): Electrically Conducting Liquid Crystalline Polymers, Mono-Substituted Polyacetylene Derivatives, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 267:1, 277-282

To link to this article: http://dx.doi.org/10.1080/10587259508034004

Mol. Cryst. Liq. Cryst. 1995, Vol. 267, pp. 277–282
Reprints available directly from the publisher
Photocopying permitted by license only

ELECTRICALLY CONDUCTING LIQUID CRYSTALLINE POLYMERS, MONO-SUBSTITUTED POLYACETYLENE DERIVATIVES

KAZUO AKAGI, HIROMASA GOTO, KIYOSHI IINO, HIDEKI SHIRAKAWA
Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki, Japan

JUNICHI ISOYA
University of Library and Information Science, Tsukuba, Ibaraki, Japan

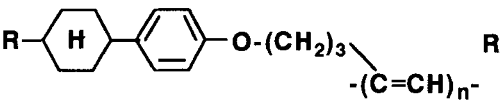
Abstract Novel side-chain liquid crystalline polyacetylene derivatives were synthesized by polymerizing substituted acetylene monomers with Ziegler-Natta and metathesis catalysts. Liquid crystallinities of the monomers and polymers were examined by means of miscibility tests, polarizing microscope and DSC measurements. Feasibility of iodine doping to the polymers was confirmed through UV-Vis absorption and ESR measurements. Changes of electronic and geometrical structures of the polymers upon the iodine doping were elucidated in terms of conjugation length of polyene chain, *cis* and *trans* forms, and spin distribution of unpaired electrons.

INTRODUCTION

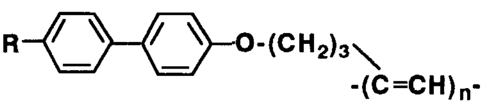
Very recently we have developed side-chain liquid crystalline conjugated polymers, mono-substituted polyacetylene derivatives.[1-6] It has been verified that application of external force such as shear stress or magnetic force into the polymers enhances an anisotropy of electrical and optical properties by virtue of orientation of main chain in accompany with alignment of the liquid crystalline side chain.[4-6] Hence, the polyacetylene derivatives with liquid crystalline group in the side chain should become candidates for advanced functional conducting polymers. In the present study, we aim to characterize these polymers in more details, especially from an aspect of thermotropic liquid crystal, and also to elucidate feasibility of chemical doping on the present polymers through UV-Vis absorption and ESR spectroscopies.

EXPERIMENTAL

Acetylene derivatives substituted with liquid crystalline groups were prepared and then polymerized with Ziegler-Natta and metathesis catalysts.[1-4] The liquid crystalline substituent of the acetylene monomer is composed of phenylcyclohexyl (PCH) moiety as a mesogenic core, a methylene chain linked with an ether-type oxygen atom, $-(CH_2)_3O$, as a spacer, and an alkyl chain, ($-C_nH_{2n+1}$, n = 2, 3, 5 - 8), as a terminal group. This monomer is abbreviated as PCHn03A, where A stands for acetylene segment. Another kind of the substituent consists of a biphenyl (BP) mesogen, a methylene chain linked with an ether-type oxygen atom as a spacer, and a *n*-pentyl group as a terminal moiety. This type of monomer is abbreviated as BP503A. The corresponding polymers are abbreviated as PPCHn03A and PBP503A, as shown below.



PPCHn03A : R = C_2, C_3, C_5 ~ C_8



PBP503A : R = C_5

RESULTS AND DISCUSSION

Liquid crystalline phase of monomers

We examined liquid crystallinity of the PCHn03A monomer. Figure 1 shows a phase diagram of mixture of PCH803A monomer and 4-(*trans*-4-*n*-propylcyclohexyl)-*n*-hexyloxybenzene, PCH306. The latter compound is known to have a nematic liquid crystalline phase and therefore used as a reference. In the miscibility phase diagram the mixture is homogeneous, irrespective of a molar ratio between two compounds. This indicates that the liquid crystalline phase of the PCH803A monomer is nematic. The result is supported by the experimental facts that the PCH803A monomer shows a mesophase in differential scanning calorimeter (DSC) and that in polarizing optical microscope it exhibits a Schlieren texture characteristic to the nematic phase. Similarly, the PCHn03A monomers with long terminal alkyl chain lengths (n = 5 ~ 7) were also confirmed to have a nematic liquid crystalline phase. It should be noted that the above mentioned mesophase of the monomer was observed only in the cooling process but not in the heating one, indicating that the monomers are monotropic liquid crystals.

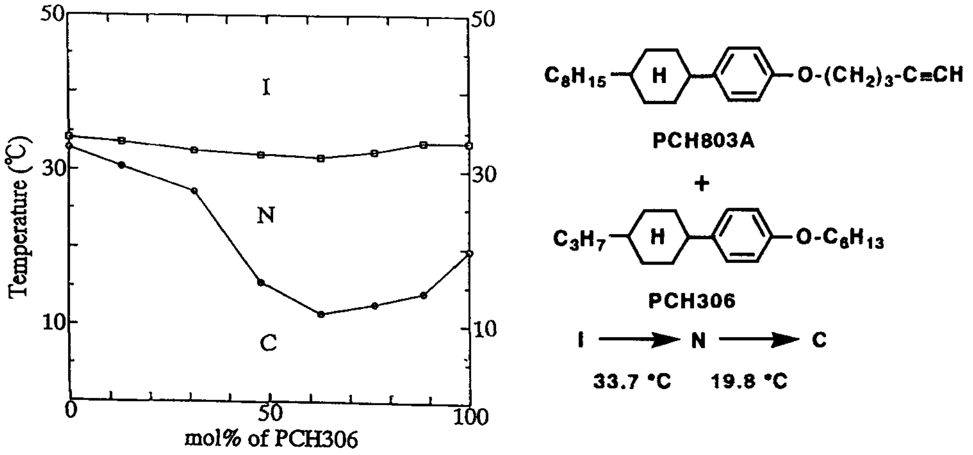


FIGURE 1 Phase diagram of mixture of PCH803A and PCH306

Liquid crystalline phases of polymers

All PCH and BP polymers with liquid crystalline group in the side chain exhibited fan-shaped textures and uniaxial conoscopic patterns in polarizing optical microscope that are characteristic to smectic A phase. The results were also supported by DSC measurements. It has been recently elucidated that the PCH and BP polymers prepared with Ziegler-Natta catalyst such as $Fe(acac)_3$-$AlEt_3$ are *cis* forms, while those with a metathesis catalyst such as $MoCl_5$-Ph_4Sn *trans* forms.[1-4] In fact, the PPCH803A prepared by the Fe-based catalyst exhibited a large exothermic peak due to a *cis-trans* isomerization at 100 ~ 176 °C in the first heating. An endothermic peak around 180 °C was hidden by the isomerization peak. In the first cooling, a peak of isotropic to liquid crystal phase transition was observed at 151 °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 ~ 142 °C. Phase transition temperatures and enthalpy changes of the some representative polymers are shown in Table I. In the PCH polymer, the enthalpy change due to the smectic to isotropic phase increases with an increase of terminal alkyl chain length. This means that the liquid crystal state is more stabilized by lengthening the alkyl chain as a terminal moiety of the liquid crystalline group. Meanwhile, the stabilization of liquid crystal state in the BP polymer is relatively small compared with the PCH polymer. Mesophases in the PPCHn03A and PBP503A polymers were observed in both heating and cooling processes. This indicates that the polymers, irrespective of the catalyst used in the polymerization, are enantiotropic liquid crystals. Here it is of interest to emphasize that the PCHn03A monomers (n = 5 ~ 8) show nematic phases, while all polymers smectic ones which have a higher order than the nematic phase. This can be rationalized with so-called

TABLE I Phase transition temperatures (°C) and enthalpy changes (J/g) in PPCHn03A and PBP503A polymers.

		First cooling					Second heating				
Cat.	Polymer	k		s_A		i	k		s_A		i
	PPCH303A		60 (0.7)		107 (4.5)			70 (0.7)		102 (3.3)	
Fe	PPCH503A		98 (1.1)		146 (6.3)			100 (1.3)		128 (6.2)	
	PPCH803A		81 (3.2)		151 (8.2)			83 (3.3)		142 (5.8)	
	PBP503A		126 (3.2)		180 (3.1)			129 (4.9)		171 (1.0)	
	PPCH303A [a]				133 (4.2)					134 (3.7)	
Mo	PPCH503A [a]				160 (6.2)					160 (4.5)	
	PPCH803A		86 (3.4)		171 (6.7)			91 (3.7)		166 (6.4)	
	PBP503A		132 (4.4)		189 (4.5)			135 (6.7)		180 (-)	

k = crystalline s_A = smectic A i = isotropic

a : No distinct DSC peak corresponding to the phase transition between crystalline and smectic A phases was observed.

polymerization effect, i.e., a higher order in molecular arrangement is generated by the polymerization of liquid crystalline monomer.

Absorption spectra and chemical doping

We examined UV-Vis absorption spectra of PCH503A monomer and PPCH503A polymer prepared with Fe-based catalyst. Absorption band at 270 ~ 280 nm, observed in both the monomer and polymer, was assigned to $\pi \rightarrow \pi^*$ transition of benzene moiety of the liquid crystalline group. Absorption band at 320 ~ 330 nm in the polymer was assigned to $\pi \rightarrow \pi^*$ transition in conjugated polyene chain. Broadening of this band implies that the polymer is composed with finite polyenes of various conjugation lengths. The results of absorption spectra for the representative polymers are summarized in Table II. The Mo-based polymer gives an absorption band located at shorter wave length (around 300 nm) than the Fe-based polymer, indicating that the former has shorter conjugation length in polyene chain than the latter.

TABLE II Absorption band, λ_{max} and intensity, ε_{max} and proton chemical shift, δ in PPCHn03A and PBP503A polymers.

Catalyst	Polymer	λ_{max} (nm)[a]	ε_{max} (x10^3)[a]	δ (ppm)[b]
	PPCH303A	324	2.0	5.98
$Fe(acac)_3$ -	PPCH503A	325	1.9	5.97
$AlEt_3$	PPCH803A	324	2.5	5.97
	PBP503A		insoluble	
	PPCH303A	301	1.4	
$MoCl_5$ -	PPCH503A	301	1.4	no value
Pn_4Sn	PPCH803A	301	1.2	
	PBP503A	305	2.6	5.94 ~ 6.14

a : Absorption band due to $\pi \rightarrow \pi^*$ transition in conjugated polyene chain
b : Chemical shift of olefinic proton in *cis* form

Absorption spectra of the Fe-based PPCH803A polymer were measured *in situ* under an iodine doping, for which the polymer had been cast onto an inner wall of quartz cell. Since an ionization potential of substituted polyacetylene is generally larger than that of non-substituted polyacetylene, it might take more time to complete the iodine doping of the polymers. Actually, there was no notable change in absorption spectrum even after three hours from an exposure of iodine to the PPCH803A polymer. After about five hours, the absorption band at 320 ~ 330 nm, assigned to $\pi \rightarrow \pi^*$ transition in conjugated polyene, slightly decreased in intensity. At the same time, new bands appeared at 420 and

700 nm. Interestingly, these bands were also observed in gas-phase doping with sulfuric acid. It is therefore evident that the two bands originate from chemically doped conjugated polyene chain and can be assigned to two kinds of electronically allowed transitions in positively charged polyene segments.

Spin state and chemical doping

Figure 2 shows ESR spectra of the PCH and BP polymers in non-doped and iodine-doped states. The ESR results are also summarized in Table III. In the non-doped state, the Fe-based PCH and BP polymers showed no signal, meanwhile the Mo-based PCH polymer showed two kinds of signals with g-values of 2.014 and 2.005. This is consistent with the above-mentioned results that the Fe-based Ziegler-Natta and the Mo-based metathesis catalysts produce *cis* and *trans* forms of mono-substituted polyacetylenes, respectively. Namely, the *cis* form is a kinetically favored product and it would be easily isomerized into a thermally more stable *trans* form during a thermal heating, chemical doping, or even polymerization using the metathesis catalyst. Such a *cis-trans* isomerization should cause defects in polyene chain, giving rise to unpaired electrons responsible for paramagnetic behavior. In practice, upon the iodine doping, the Fe-based PCH and BP polymers showed sharp ESR signals with g-values of 2.006 and 2.003, respectively. On the other hand, in the Mo-based polymer doped with iodine, the lower field signal (g = 2.014) slightly decreases in intensity and the higher field signal (g = 2.005) increases, resulting in overlapped signals.

The peak width, ΔH_{pp}, is larger by 3 ~ 5 times and spin density is smaller by 2 ~ 4 order than those of iodine-doped polyacetylene.[7] Such a large peak width suggests that

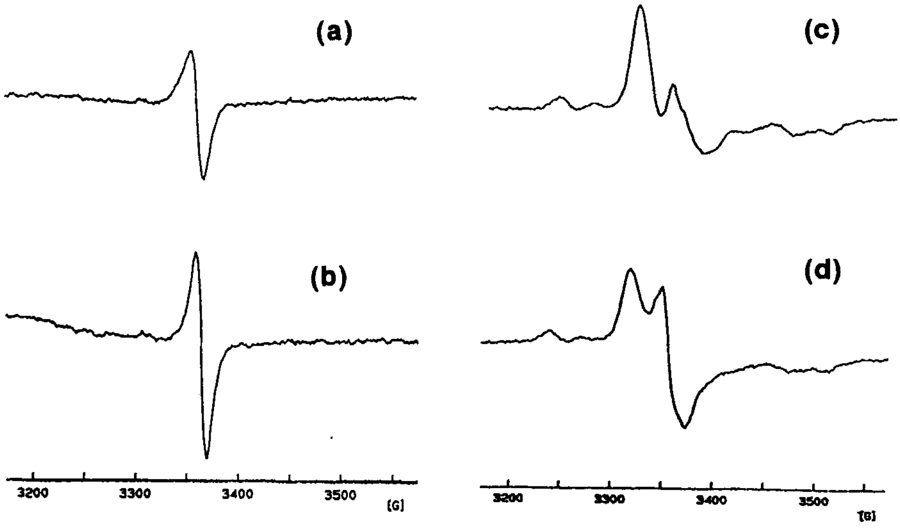


FIGURE 2 ESR spectra measured at room temperature. (a) : I_2-doped PPCH503A (Fe), (b) : I_2-doped PBP503A (Fe), (c) : non-doped PPCH503A (Mo), (d) : I_2-doped PPCH503A (Mo).

TABLE III ESR results of the iodine-doped PCH and BP polymers.

Polymer	Catalyst	g-Value	ΔH_{pp}[a] (Gauss)	$\Delta H_{1/2} / \Delta H_{pp}$	Spin density (spin / g)	y-Value[b]
PPCH503A	Fe	2.006	15.1	2.05	3×10^{15}	0.065
PBP503A	Fe	2.003	11.0	2.36	1×10^{15}	0.097
PPCH503A	Mo	2.014, 2.005	—[c]	—[c]	2×10^{17}	0.028

a : Peak to peak width in differential curve of signal. b : Dopant concentration defined as $[(CHCR)^{+3y}(I_3^-)_y]_x$, where R is liquid crystal group. c : Two peaks are overlapped.

the unpaired electrons in the substituted polyacetylene tend to be more localized, probably due to an increase of non-planarity of the polyene chain. From a view point of electrical transport phenomenon, it can be argued that the present polymers have a lower mobility and a lower concentration of carrier. This may account of the lower electrical conductivity of the substituted polyacetylenes including the present PCH and BP polymers.

CONCLUSION

We confirmed that two kinds of mono-substituted polyacetylene derivatives synthesized with the Fe-based Ziegler-Natta catalyst or the Mo-based metathesis catalyst were enantiotropic smectic A liquid crystalline polymers. The longer terminal alkyl chain linked with the phenylcyclohexyl or biphenyl mesogenic core afforded more stabilization in the liquid crystal states of the polymers. *Cis* and *trans* structural dependencies of the polymers on polymerization catalyst were rationalized with both DSC and ESR measurements. Chemical doping on the polymers was found to be feasible, which implies that the present polymers should be promising as novel functional conducting materials.

ACKNOWLEDGMENTS

This work was supported by Grant-in-Aid for Scientific Research from Ministry of Education, Culture and Science of Japan, and Iketani Science and Technology Foundation of Japan.

REFERENCES

1. S.-Y. Oh, K. Akagi, H. Shirakawa, and K. Araya, *Macromolecules*, **26**, 6203 (1993).
2. K. Akagi, S.-Y. Oh, H. Goto, Y. Kadokura, and H. Shirakawa, *Proc. of the 3rd IUMRS Int. Conf. Ad. Mat., Symposium Q*, (1993), in press.
3. H. Shirakawa, Y. Kadokura, H. Goto, S.-Y. Oh, K. Akagi, and K. Araya, *Mol. Cryst. Liq. Cryst.*, (1994), in press.
4. K. Akagi, H. Goto, Y. Kadokura, H. Shirakawa, S.-Y. Oh, and K. Araya, *Synth. Met.*, (1995), in press.
5. K. Akagi, S.-Y. Oh, H. Shirakawa, and T. Nishizawa, *Polym., Prep. Jpn.*, **42**, 698, (1993) .
6. K. Akagi, H. Goto, H. Shirakawa, T. Nishizawa, and K. Masuda, *Synth. Met.*, (1995), in press.
7. D. Davidov, S. Roth, W. Neuman, and H. Sixl, *Solid State Comm.*, **52**, 375, (1984).