This article was downloaded by: [University of Tennessee At Martin] On: 07 October 2014, At: 18:38 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Synthesis and Properties of Liquid Crystalline Polythiophene and Polythienylenevinylene Derivatives

Itaru Osaka^a, Hiromasa Goto^a, Kikuo Itoh^b & Kazuo Akagi^a

^a Institute of Materials Science, University of Tsukuba , Tsukuba, Ibaraki, 305-8573, Japan

^b Tsukuba Magnet Laboratory, National Research Institute for Metals, Tsukuba, Ibaraki, 305-0003, Japan

Published online: 27 Oct 2006.

To cite this article: Itaru Osaka , Hiromasa Goto , Kikuo Itoh & Kazuo Akagi (2001) Synthesis and Properties of Liquid Crystalline Polythiophene and Polythienylenevinylene Derivatives, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 339-346, DOI: 10.1080/10587250108025312

To link to this article: <u>http://dx.doi.org/10.1080/10587250108025312</u>

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <u>http://www.tandfonline.com/page/terms-and-conditions</u> Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 339-346 Reprints available directly from the publisher Photocopying permitted by license only

Synthesis and Properties of Liquid Crystalline Polythiophene and Polythienylenevinylene Derivatives

ITARU OSAKA^a, HIROMASA GOTO^a, KIKUO ITOH ^b and KAZUO AKAGI^a

^aInstitute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305–8573, Japan and ^bTsukuba Magnet Laboratory, National Research Institute for Metals, Tsukuba, Ibaraki 305–0003, Japan

Liquid crystalline polythiophene (LC-PTs) and polythienylenevinylene (LC-PTVs) derivatives with various length of methylene spacer in the LC substituents were synthesized. LC-PTs were prepared through dehalogenative polycondensation using Ni(0) complex, and LC-PTVs through Stille reaction followed by Heck reaction. The polymers showed enantiotropic smectic phase. Both LC-PTs and LC-PTVs were fluorescent with greenish yellow and/or green colors. The polymers were macroscopically aligned under magnetic field of 10 Tesla. Alignment of the polymers was confirmed by polarizing optical microscope, X-ray diffraction and polarized infrared spectra. The aligned polymers showed not only anisotropic electrical conductivity but also dichroic fluorescence. It is found that the LC conjugated polymers synthesized here are promising materials with linearly polarized luminescence.

Keywords: polythiophene; polythienylenevinylene; liquid crystallinity; anisotropic conductivity; dichroic fluorescence

INTRODUCTION

Polythiophene (PT) derivatives are representative five-membered conjugated polymers and regarded as promising materials for advanced electrical and optical devices. The alignment of conjugated polymer main chain is one of the key factors to enhance the electrical conductivity. Introduction of liquid crystals into π -conjugated polymer is expected to afford anisotropies in both electrical and optical properties. This is because the orientation of liquid crystalline (LC) side chain could lead the macroscopic alignment of the conjugated backbone.

LC polyacetylenes previously synthesized [1-3] exhibited an enhancement and an anisotropy in electrical conductivity after magnetically forced alignment. Meanwhile the LC-PTs [4,5] and poly-*p*-phenylene derivatives (PPPs) [6,7] are anticipated to exhibit dichroic luminescence as well as anisotropic conductivity. In this work, we report the synthesis and properties of LC-PT and LCpolythienylenevinylene (PTV) derivatives with LC substituents such as cyanobiphenyl (CB) and phenylcyclohexyl (PCH) mesogenic cores. The polymers synthesized were subjected for macroscopic alignment under magnetic field.

SYNTHESIS

Synthesis of 2.5-Dibrominated Thiophenes with CB Type LC Side Chain

3-Thiophenemethanol was brominated at 2 and 5 positions of thiophene ring by using N-bromosuccineimide (NBS) and dichloromethane. The brominated thiophenemethanol was linked with 1,n-dibromoalkane (n =6, 8, 10, 12) through etherification, to give nT. CBnT was synthesized by etherification of nT and 4-cyano-4'-hydroxybiphenyl using K₂CO₃ and KI (SCHEME 1).

Synthesis of 2,5-Dibrominated Thiophenes with PCH Type LC Side Chain

3-Thiopheneacetic acid was brominated at 2 and 5 positions of thiophene ring. PCHnOH was synthesized by etherification of n-bromo-1-alkanol (n = 6, 8, 10, 12) and 4-(*trans*-4'-*n*-pentylcyclohexyl)phenol using K₂CO₃ and KI, and then coupled with brominated thiopheneacetic acid using dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP), giving PCHnT (SCHEME 2).

Polymerization

Polymerizations of CBnT and PCHnT were carried out through dehalogenative polycondensation using bis(1,5-cyclooctadiene)nickel



SCHEME 1 Synthetic route of CBnT (n = 6, 8, 10, 12)



SCHEME 2 Synthetic route of PCHnT (n = 6, 8, 10, 12)





[Ni(cod)₂], and 2,2'-bipyridine [bpy], yielding PCBnT and PPCHnT, respectively (SCHEME 3, upper).

CBnT and PCHnT were coupled with tributyl(vinyl)tin, tris(dibenzylideneacetone)dipalladium(II) $[Pd_2(dba)_3]$ and tri(furyl)phosphine $[P(furyl)_3]$ as catalysts according to Stille reaction, and subsequently polymerized through Heck reaction using palladium acetate $[Pd(OAc)_2]$ and tri(o-tolyl)phosphine $[P(o-Tol)_3]$ as catalysts, yielding PCBnTV and PPCHnTV, respectively (SCHEME 3, lower).

RESULTS AND DISCUSSION

Chemical. optical. electrical and thermal properties of the polymers All polymers synthesized were fusible and soluble in organic solvents. Their chemical, optical and electrical properties are summarized in Table I. The molecular weights of the polymers were evaluated through GPC calibrated by polystyrene standards. The degrees of polymerization of LC-PTs were larger than those of LC-PTVs. Thus the absorption bands due to π - π * transition of main chain of LC-PTs were located at longer wavelength than those of LC-PTVs. Electrical conductivities of the iodine doped polymers were $10^{-8} - 10^{-5}$ S/cm.

The polymers exhibited greenish-yellow fluorescence at 490 - 530 nm in CHCl₃. Emission maxima of LC-PTs were observed at longer

14
r 20
tobe
ŏ
01
18:38
at
tin]
Mar
At
ennessee
of Te
ersity
niv
Ð
by
aded
wnlo
Do

valuated by using quinine sulfate	quantum yield e	Fluorescence	thoulder.	, sh:	from Mn.	calculated	olymerization	Degree of p
G (-) - S _B 61 (52) S _A 73 (65)		2.4	470	3.41	366	10	5500	PPCH12TV
G (-) - S _B 56 (51) S _A 65 (63)	1.5×10 ⁴	2.5	485	3.57	353	15	8200	PPCH10TV
G (-) - S _B 84 (74) S _A 90 (82)	•	3.5	480	3.17	373	10	5000	PPCH8TV
G 65 (55) S _A 80 (70) I	5.9×10 ⁴	3.2	495	4.10	378	10	4800	PPCH6TV
G 45 (40) S _A 62 (60) I		5.0	477	3.39	360 (sh)	6	4300	PCB12TV
G 60 (55) S _A 75 (68) I	2.7×10 ⁻⁵	3.6	494	3.60	360	15	7200	PCB10TV
G 70 (65) I	ı	2.7	485	3.61	355 (sh)	7	3000	PCB8TV
G 60 (55) I	•	3.0	493	3.59	364	80	3400	PCB6TV
G (-) - S _B 73 (68) S _A 95 (91)	ı	1.4	508	3.58	366	12	6500	PPCH12T
G (-) - S _B 56 (52) S _A 61 (59)	2.0×10 ⁴	7.6	527	3.78	395	38	20000	PPCH10T
G (-) - S _B 62 (58) S _A 75 (73)	ŀ	4.0	518	3.71	373	16	7800	PPCH8T
G 70 (60) S _A 82 (72) I	1.0×10 ⁴	7.6	533	4.19	401	76	36000	РРСН6 Т
G 60 (55) S _A 75 (68) I	•	2.5	519	3.66	364	14	6700	PCB12T
G 60 (55) S _A 98 (94) I	3.5×10*	6.3	536	3.76	400	25	11000	PCB10T
G 36 (30) S _A 60 (45) I	·	5.3	517	3.61	372	6	3700	PCB8T
G 35 (30) S _A 70 (48) I		3.5	500	3.50	350 (sh) ^b	13	5200	PCB6T
Phase transition temperatures (°C) ^{*,f}	σ (S/cm) ⁴	, (%) Ф	PL (nm)	log e	γ_ (nm)	DP.	Mn	polymers

TABLE I Properties of LC-PTs and LC-PTVs

' Values without standard sample. 'Electrical conductivity after indine doping. 'G, glassy, SA; smeetic A, SB; smeetic B, I; isotropic. with parentheses correspond to heating and cooling process, respectively.



100 µm

Polarizing optical micrograph of PCB10T at FIGURE 1 88 °C in cooling process. See Color Plate XX at the back of this issue.



Polarizing optical micrograph of PCB10T at room FIGURE 2 temperature after magnetically forced alignment. See Color Plate XXI at the back of this issue.



FIGURE 3 Polarized PL spectra of aligned PPCH10T

wavelength than those of LC-PTVs, as expected from the behavior in UV-Vis absorption spectra. The fluorescence intensity of LC-PTs was larger than that of LC-PTVs. Fluorescence quantum yields were evaluated by using quinine sulfate as a standard sample. Excitation wavelength used for both the polymers and quinine sulfate was 366 nm. The values of quantum yields were 1.4 - 7.6 %.

The phase transition temperatures are also listed in Table I. Measurements indicate that the polymers with CB type LC group have enantiotropic smectic A phase. Those with PCH type LC group have smectic A and B ones, although PCH6T with methylene spacer of 6 show only smectic A phase. Similar results were observed in LC-PTV, except PCB6TV and PCB8TV that exhibit no mesophase. Figure 1 shows a typical fan-shaped texture of PCB10T.

Magnetically forced alignment of the polymers

In order to realize polarized luminescence and anisotropic electrical conductivity, we carried out magnetically forced alignment of the polymers. Magnetic field (H) of 10 Tesla was applied to the polymers

under LC temperature during both heating and cooling processes.

Figure 2 shows polarizing optical microscope (POM) of aligned polymer of PCB10T. It is clear that domains were aligned parallel to the direction of *H*. Measurements of XRD, polarized IR and UV-Vis spectra indicated that LC side chains are aligned parallel to *H* and consequently the main chains are aligned perpendicular to *H*. The aligned polymers showed an anisotropy in electrical conductivity, where the ratio of perpendicular to parallel conductivity ($\sigma_{1/} \sigma_{n}$) was 2.0 - 8.5. Note that σ_{\perp} stands for conductivity perpendicular to the magnetic field, i.e., parallel to main chain, and hence σ_{n} stands for perpendicular to main chain. Lastly, the aligned polymer films of LC-PTs and LC-PTVs showed dichroic fluorescence with dichroic ratios of 2.0 - 3.8 and 1.4 - 1.8, respectively, as shown in Figure 3.

CONCLUSION

A series of LC-PTs and LC-PTVs were synthesized. The polymers exhibited dichroic fluorescence with greenish-yellow color when they were macroscopically aligned by magnetic field. It is suggested that they are useful for novel optical advanced materials with polarized luminescence.

References

- [1] S.-Y. Oh, K. Akagi, H. Shirakawa, K. Araya, Macromolecules, 26, 6203 (1993).
- [2] K. Akagi, H. Goto, Y. Kadokura, H. Shirakawa, S. -Y. Oh, K. Araya, Synth. Met., 69, 13 (1995).
- [3] K. Akagi, H. Goto, K. Iino, H. Shirakawa, J. Isoya, Mol. Cryst. Liq. Cryst., 267, 277 (1995).
- [4] R. Toyoshima, M. Narita, K. Akagi, H. Shirakawa, Synth. Met., 69, 289 (1995).
- [5] I. Osaka, S. Shibata, R. Toyoshima, K. Akagi, H. Shirakawa, Synth. Met., 102, 1437 (1999).
- [6] J. Oguma, K. Akagi, H. Shirakawa, Synth. Met., 101, 86 (1999).
- [7] K. Akagi, J. Oguma, S. Shibata, R. Toyoshima, I. Osaka, H. Shirakawa, Synth. Met., 102, 1287 (1999).