

Original fundamental ideas and the first experiments

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- 1) Development of chiral liquid crystal polyacetylene derivatives for ferroelectric liquid crystal polyacetylene.
- 2) Electrochemical polymerization in liquid crystals.
- 3) Electrochemically driven change in conjugated polymers prepared in cholesteric liquid crystals.
- 4) Polycondensation in liquid crystal solvent as a new type of asymmetric reaction.

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p5. (1993, June), Polymerization

II) Electrochemical polymerization in liquid crystals

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IV) The Stille-type polycondensation of achiral monomers in cholesteric liquid crystal for obtaining chiroptical polymers, and confirmation of the optical activities

p 13. (2003, April) Asymmetric polycondensation reactions in liquid crystals.

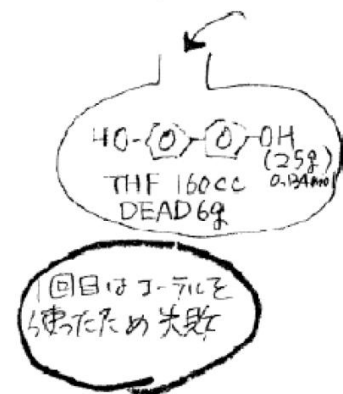
p 14. (2003, October) Measurements of optical activities of the polymers prepared by the Stille coupling reaction in cholesteric liquid crystal solvent.

Goto, H., *Res. Lab Note, U. Tsukuba* 1993, **5**, 5069 (1993, January)

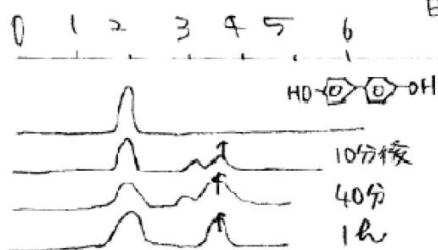
Synthesis of a precursor compound of chiral liquid crystal polyacetylene derivative

No. 5069
Date

F.L.Cの分析

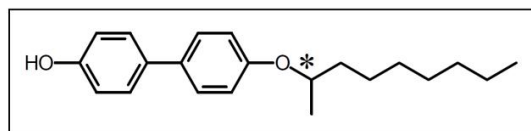
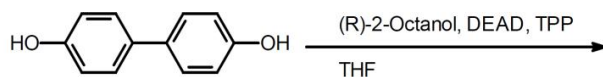


1. アルカン → π* で
オレンジ色
2. Ph₃P E 20cc THF に 2 mL (9.2g)
drop by drop 30min.
すると、オレンジが消え、白い沈殿と赤い
うすまじり色。
3. R-171-HL 5ml E drop
7:30. 色は黄緑色で、
だんだんと黄緑がうすくなる。
時間と共に色は消える。



3.66分はエーテル?
↓
エーテル

GO 0691-1
GO 0569-1.
GO 05069-

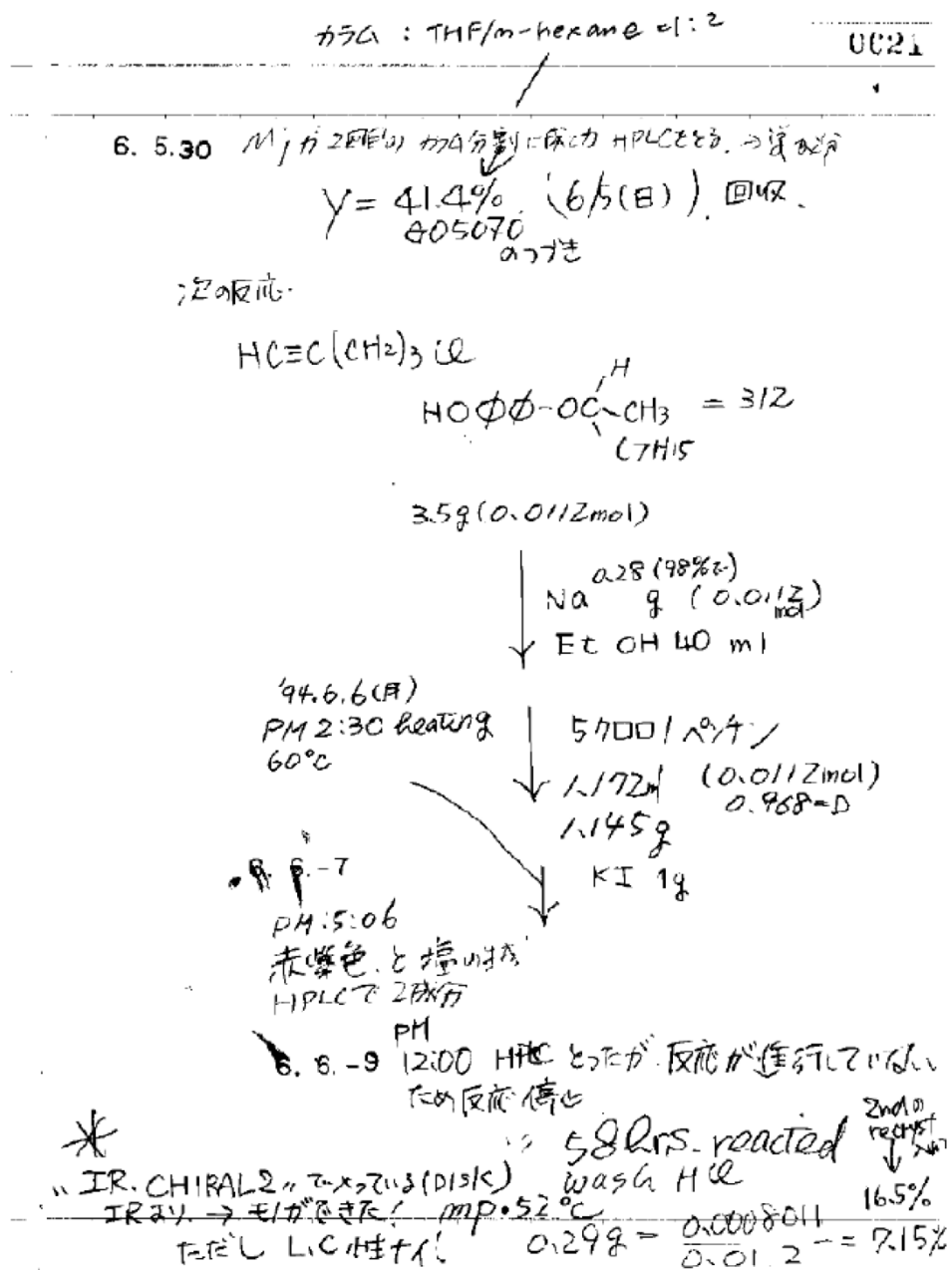


DEAD = diethylazodicarboxylate, TPP = triphenyl phosphine, THF = tetrahydrofuran

In the first experiment, the reaction did not occur because ether was employed in the reaction (Goto, H., *Res. Lab Note, U. Tsukuba* 1993, **5**, 5054). This time, the reaction in tetrahydrofuran (THF) was successful.

Goto, H., Res. Lab Note, U. Tsukuba 1993, 6, 0621 (1993, May)

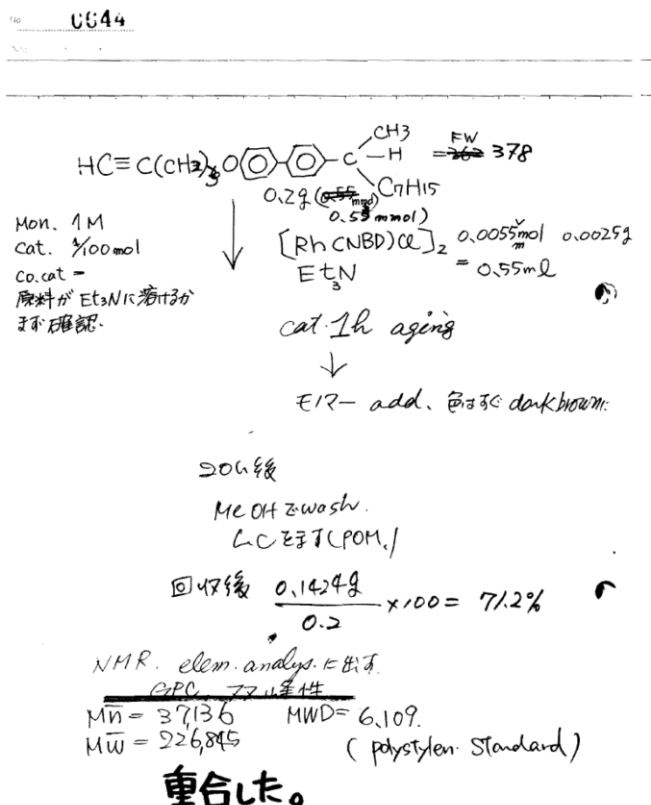
Synthesis of a monomer of chiral liquid crystal polyacetylene derivative



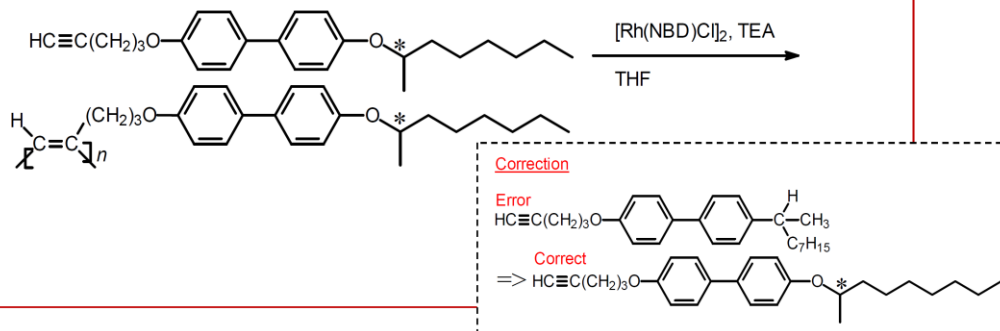
Content of the experiment: Purification of a precursor of chiral liquid crystal polyacetylene derivative and synthesis for chiral liquid crystal polyacetylene derivative as a monomer.

Goto, H., *Res. Lab Note, U. Tsukuba* 1993, **6**, 0644 (1993, June)

Polymerization for obtaining a chiral liquid crystal polyacetylene derivative



Content of the experiment: Polymerization of the monomer of chiral liquid crystal polyacetylene derivative. The polymer thus obtained shows liquid crystal phase with spiral texture.



Goto, H., *Res. Lab Note, U. Tsukuba* 2000, **24**, 2401 (2000, Dec)

Electro-synthesis in liquid crystals

DEC. - 4 2000

LC B6 = 263.38	3g	0.011 mol	//	3g	LC/CR-Pink
<small>CPK Pur 1506-Pink</small>					0.02
$N^{\oplus} = 943$	40	0.5g 0.2g	2.1×10^{-4} mol	//	
pyrrole 87.09	0.05g	(7.4×10^{-4})	//		
TBAP = 341.90	0.001g	(2.9×10^{-6})	//		

6CB/1mM TBAP

Py: 1:4:14:6CB: TBAP 3.77×10^{-3} $\text{Py}/6\text{CB} = 0.02 \text{ End}$

= 1:0.3:14: 3.9×10^{-3} $\text{Py}/6\text{CB} = 0.02/1/0.$

Content of the experiment: Preparation of liquid crystal electrolyte solution containing pyrrole for electrochemical polymerization.

Goto, H., *Res. Lab Note, U. Tsukuba* 2000, **24**, 2416 (2000, December)

Electro-synthesis in liquid crystals (sandwich cell method)

no 2416
 DEC. 23 2000
 pyrrole N* dopant electro-polymerization
 0.04A 0.05A 最初
 0.5V 0.1V
 12/23 PM 5:00~
 17/23 PM 5:00~

LCB6	3g
N* dopant	0.13g
pyrrole	0.06g
TBAP	0.01g

17/23 PM 5:00~
 9:00 the colour doesn't change?

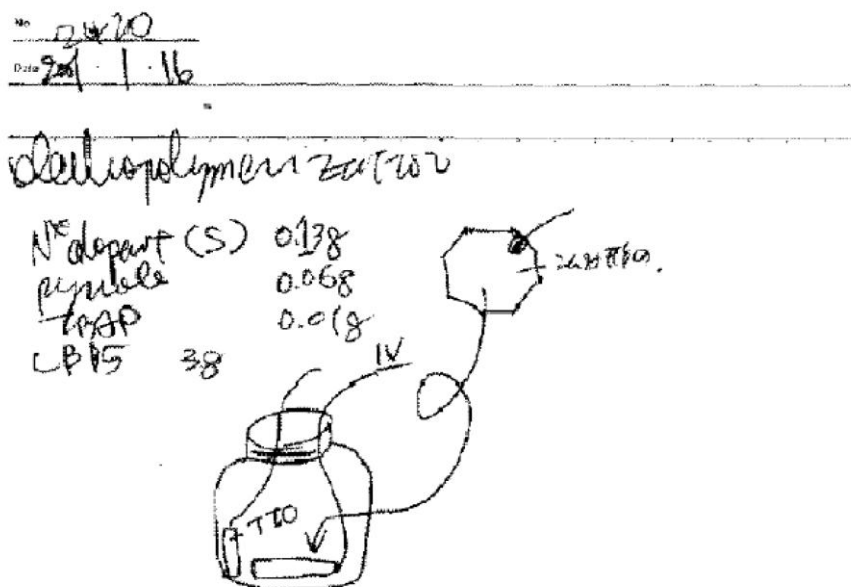
Content of the experiment: Sandwich-cell liquid crystal electrochemical polymerization for polymerization of pyrrole..



Polypyrrole film deposited on indium-tin-oxide (ITO) coated glass prepared by the sandwich-cell electrochemical polymerization in liquid crystal electrolyte solution developed firstly in 2000 (23 Dec, 2000).

Goto, H., *Res. Lab Note, U. Tsukuba* 2001, **24**, 2420 (2001, January)

Electro-synthesis in liquid crystals (proto-type electrochemical polymerization in liquid crystal)



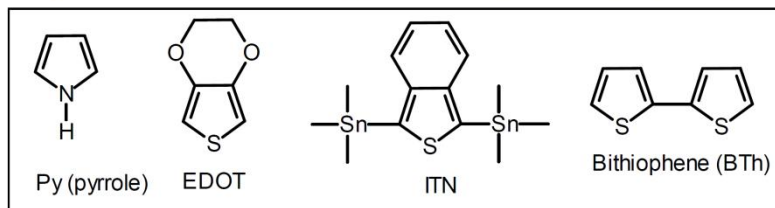
Content of the experiment: The proto-type electrochemical polymerization in liquid crystals.

Goto, H., *Res. Lab Note, U. Tsukuba* 2001, **304**, 3083 (2001, June)

Electro-synthesis in liquid crystals

No. 3083		Date 16.6.8	
実験用のNLC-セル			
G030831 (S)	G030832 (R)		
Py 0.04g			
6CB 1g			
TBAP 0.01g			
Binol (R) 0.02g	Binol (R)		
G030833 (S)	G030834 (R)		
EDOT 0.04g			
6CB 0.5g 1g	1g		
TBAP 0.01g			
Binol (S) 0.02	Binol (R)		
G030835 (S)	G030836 (R)		
ITN 0.006g	"		
6CB 0.5g			
TBAP 0.01g			
Binol (S) 0.02	Binol (R)		
G030837 (S)	G030838 (R)		
bithiophene 0.04g	"		
6CB 0.5g			
TBAP 0.01g			
Binol (S) 0.02	(R)		

Content of the experiment: Polymerization of pyrrole in N* (cholesteric) liquid crystal electrolyte solution.



Goto, H., Res. Lab Note, U. Tsukuba 2004, **30**, 3093 (2004, June)

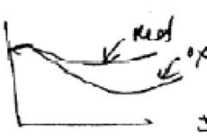
Electro-synthesis in liquid crystals (a completed method)

VOL. 3093
2004. 6. 15
16.6.17

~~E4772~~ ~~6CB~~ ~~TBAP~~ ~~BINDL (S) OR (R)~~ 0.04g
 6CB 0.5g
 TBAP 0.0005g
 BINDL (S) OR (R) 0.02g

E4772 (R) の合成
~~3.85V~~ AM12.15 ~
 4.85V
 TBAPを24000cc 674031100

C4 { BTR... pristine
 BTRPK... +20
 BTRPK2 -2V,
 BTRPK2 +2V



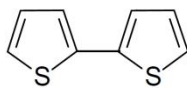
2.4 x 10⁻⁴ mol
 1.9 x 10⁻³ mol
 1.5 x 10⁻⁶ mol
 2.1 x 10⁻⁵ mol

16.6.17

E4772 = 166.25 0.04g
 6CB = 269.38 0.5g ←
 TBAP = 341.91 0.0005g
 BINDL (S) OR (R) 0.02g
 = 993.40

BT(3)
~~0.48M~~ ~~0.8M~~ 2.4 x 10⁻⁴ mol
~~0.5g~~ 1.9 x 10⁻³ mol
 3mM 1.5 x 10⁻⁶ mol
 0.042M 2.1 x 10⁻⁵ mol

Content of the experiment: Polymerization of bithiophene in N* (cholesteric) liquid crystal electrolyte solution. Note that the date of 16.6.17 in the Japanese almanac corresponds to 15 June, 2004.



ビチオフェン=Bithiophene (BTh)

Goto, H., *Res. Lab Note, U. Tsukuba* 2004, **31**, 3105 (2004, June)

Measurements and confirmation of chiroptically active electro-chromism

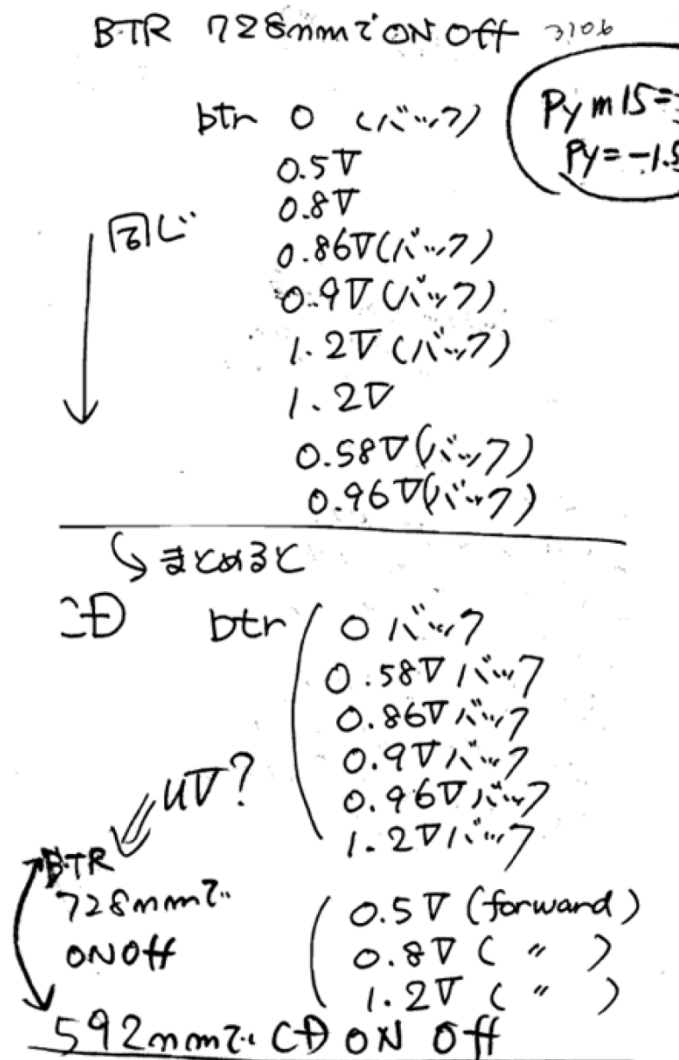
$\text{CD} / \text{V} \text{ E}$ の測定が 3105
 E-DOT (R) \leftarrow $\text{UV} \rightarrow \text{UV}$
 -0.3V
 0.2V
 0.5V
 0
 -0.2V (1.1V) \rightarrow LED
 (edmo2b) ON/OFF!
 E-DOT
 UV (R) \leftarrow $\text{6.2 mm} \times \text{2 mm} \times \text{1 mm}$ \leftarrow CD, ON/OFF
 edmo3 (forward)
 edo2 (forward)
 edo5 (*)
 EDQ (back)
 EDMmo2b (-0.2V)
 EDM3b (-0.3V back)

深夜 = Midnight

Content of the experiment: Electrospectroscopy measurements in circular dichroism (CD) for poly(3,4-ethylenedioxythiophene) (PEDOT*, * = chiral) synthesized in liquid crystals. The PEDOT was prepared by the method described in Goto, H., *Res. Lab Note, U. Tsukuba* 2001, **304**, 3083 (2001, June)

Goto, H., *Res. Lab Note, U. Tsukuba* 2004, **31**, 3106 (2004, June)

Measurements and confirmation of chiroptically active electro-chromism



Content of the experiment: Electrospectroscopy measurements in circular dichroism (CD) for polybithiophene (PBTh*, * = chiral) synthesized in liquid crystals. The PEDOT was prepared by the method described in Goto, H., *Res. Lab Note, U. Tsukuba* 2001, **304**, 3083 (2001, June)

Goto, H., *Res. Lab Note, U. Tsukuba* 2003, **31**, 2965 (2003, April)

Asymmetric polycondensation reactions in liquid crystals.

2003.4.7 (A) 2003.4.21 (A)

LC 中重合

EtO2C-C6H4-SnMe3

SnMe ₃ -C ₆ H ₄ -C ₆ H ₄ -SnMe ₃	0.1g	0.0805g
Ar-C ₆ H ₄ -Br	0.085g	0.0684g
LC - CR ₂ S ⁺	1g	0.805
Pd(PPh ₃) ₄	0.003g	0.002

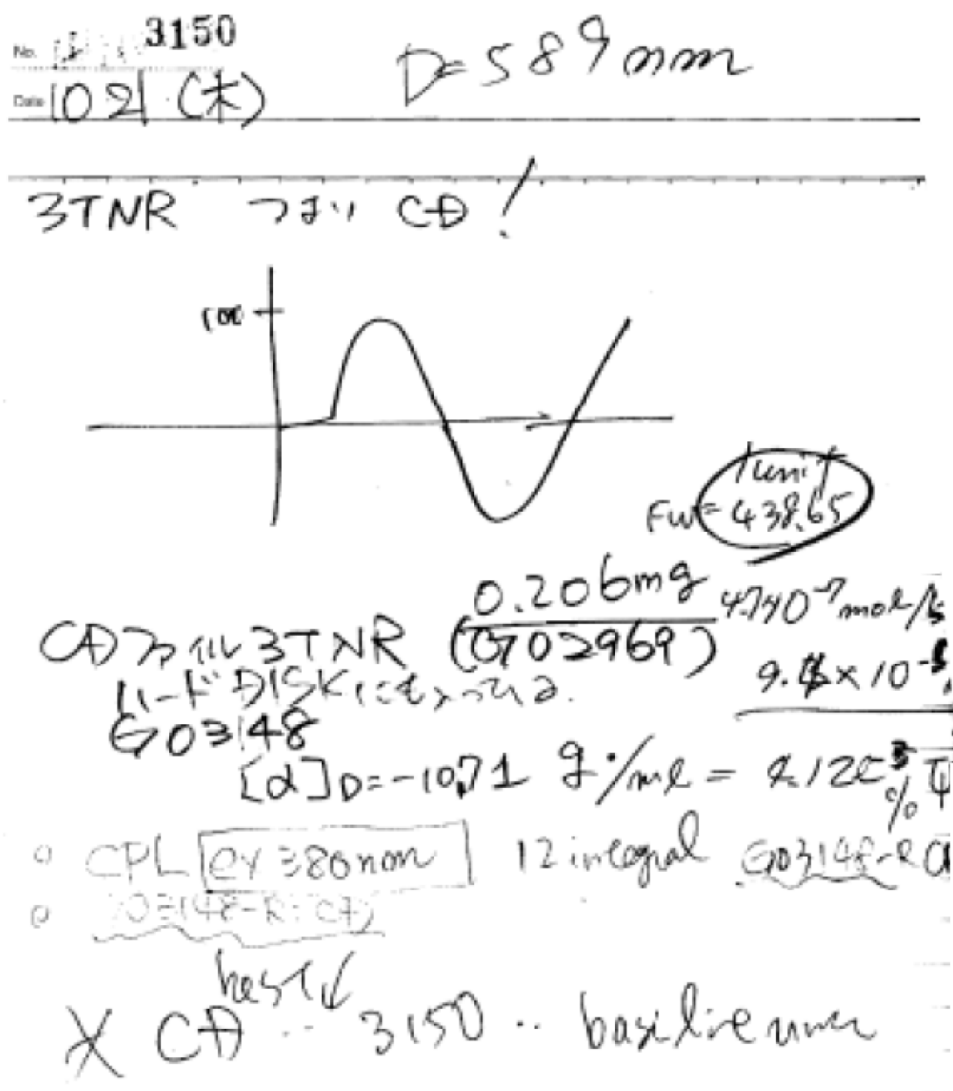
(1) 2969-1 (R) 2
 (2) 2969-2 (S) 2

2003.4.7 AM 2:30
 ① 24h wash / acetone 後 24h 乾燥 70°C
 ② wash again in Acetone

Content of the experiment: Stille-type polycondensation reaction in cholesteric liquid crystals was carried out for the first time after unsuccessful attempt on 14 and 21 March, 2003.

Goto, H., *Res. Lab Note, U. Tsukuba* 2003, **31**, 3150 (2003, October)

Measurements of optical activities of the polymers prepared by the Stille coupling reaction in cholesteric liquid crystal solvent.



Content of the experiment: The CD and optical rotation measurements of the polymer prepared in cholesteric liquid crystal by the Stille type polycondensation.