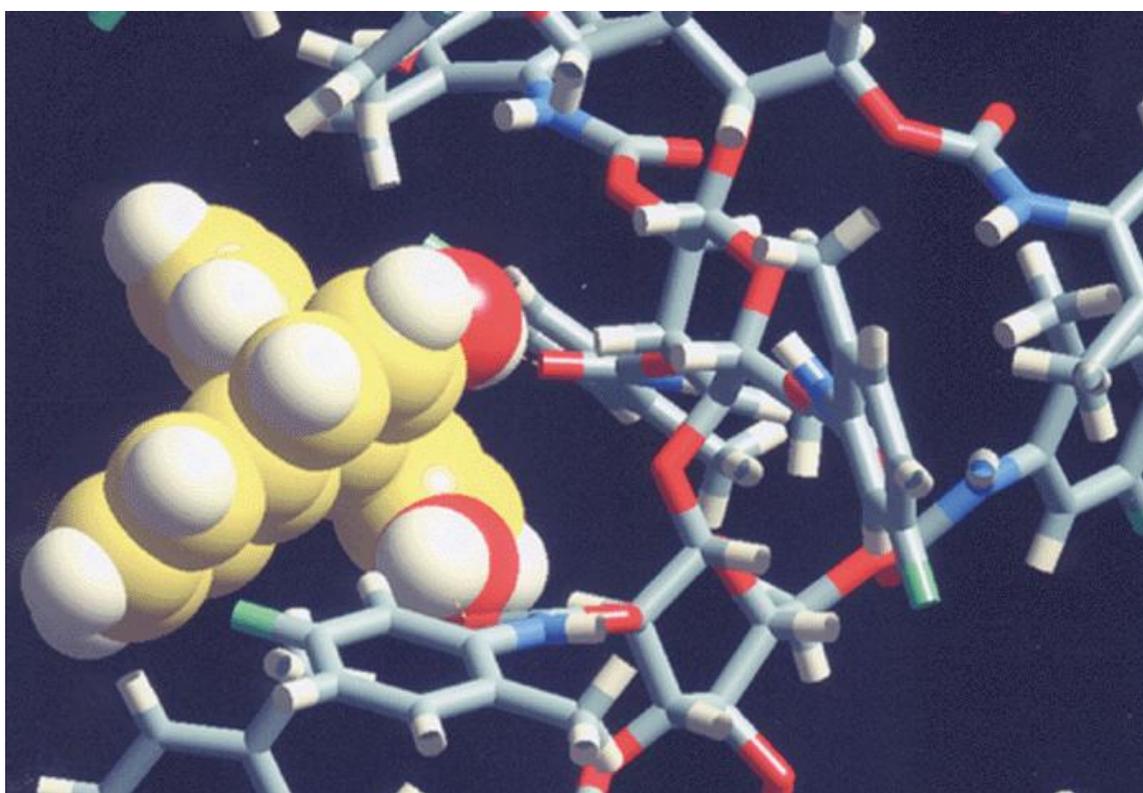


# General polymer to Smart polymer

~Introduction of polymer chemistry~



- ◆ 1.Introduction
- ◆ 2.Organic Synthetic Application
- ◆ 3. Reversible polymers for Smart polymer
- ◆ 4.Summary

# 1. Introduction

Reference: 日本化学会 実験化学講座化学講座 4 基礎編IV 2003 丸善  
日本化学会 実験化学講座 28 高分子 1992 丸善  
井上祥平 高分子合成化学 改訂版 2011 裳華房  
蒲池幹治 高分子化学入門 改訂版 2006 NTS



## 1-1. What is polymer

### • Definition by IUPAC:

A molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass.

• Generally measure of molecular weight is about over 10,000.

### Notes

1. In many cases, especially for synthetic polymers, a molecule can be regarded as having a high relative molecular mass if the addition or removal of one or a few of the units has a negligible effect on the molecular properties. This statement fails in the case of certain macromolecules for which the properties may be critically dependent on fine details of the molecular structure.

2. If a part or the whole of the molecule has a high relative molecular mass and essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass, it may be described as either **macromolecular** or **polymeric**, or by **polymer** used adjectivally.

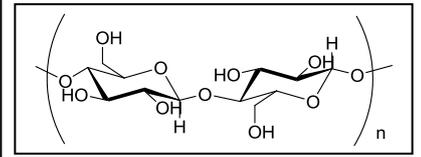
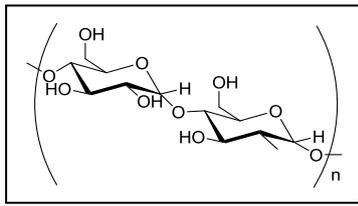
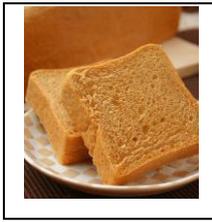
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### • Compared with Organic chemistry(so-called)

#### Polymer chemistry

- Handling macromolecular
- Product property depend on not only construction.(functional group • structure ...etc)
- Be decided only after the distribution of molecular weight is specified, so dynamic and the thermodynamic in the solid and the solution state characteristic is greatly different from the monomeric substance.

## 1-2. Examples of Polymer



Food : starch....amylose

(composed by α 1→4 D-glucose)

Housing: wood fiber....cellulose

(composed by β 1→4 D-glucose)



Artificial



Clothing: Silk

(composed by amino acid)

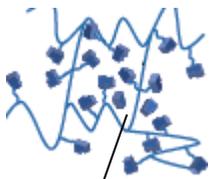
Rayon(artificial silk)

(composed by regenerated cellulose)

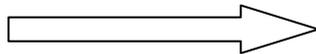


Almost all things in this picture are polymer

## 1-3. Fundamental knowledge



Hard to separate into a monomolecular group



Polymer is analyzed in the assembly,

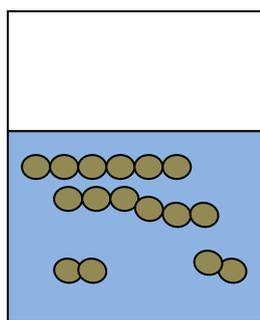
Average molecularweight

- Mn (number-average molecular weight)  

$$= \frac{\sum_i N_i M_i}{\sum_i N_i}$$
- Mw (weight-average molecular weight)  

$$= \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

e.g.)



●: oligomer

(MW=1,000)



$M_n=4,000$ ...for calculation

$M_w=5,000$ ...for dealing with physical property

$M_w/M_n=1.25$

•  $M_w/M_n$  : poly dispersity index

Polymer have no dispersion :  $M_n = M_w$  ( $M_w/M_n=1$ )

Polymer have dispersion :  $M_n < M_w$

indicator of reaction type

- Radical polymerization :  $M_w/M_n =$  about 2~3
- condensation polymerization :  $M_w/M_n =$  about 2
- Living polymerization :  $M_w/M_n =$  about 1.1

### ○Determination of molecular weight

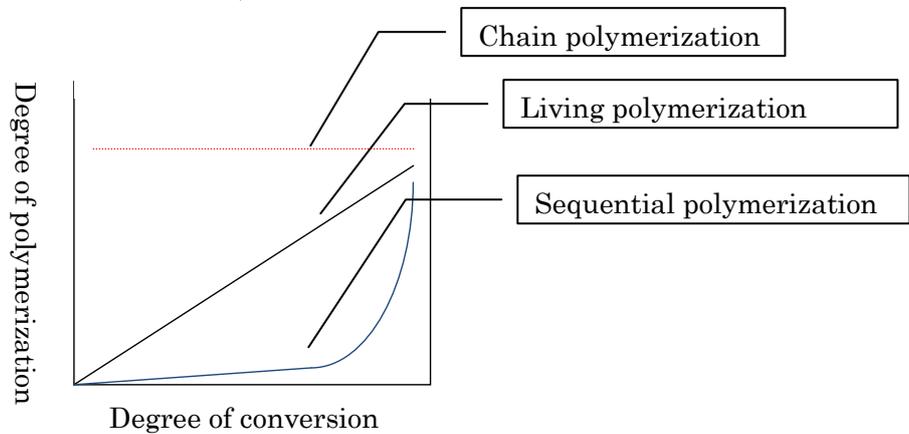
Measurement	Sort of average	Molecular weight range	instrument
<b>Terminal group determination</b>	$M_n$	$10^3 \sim 10^5$	<b>NMR</b>
Cryoscopic method	$M_n$	$< 3,000$	Cryoscopic apparatus
Ebullioscopic method	$M_n$	$< 3,000$	Ebullioscopic apparatus
Osmometry	$M_n$	$10^4 \sim 10^6$	osmometer
<b>Mass spectrometry</b>	$M_n$	$< 10^5$	<b>MALDI-TOF MASS</b>
<b>Light scattering method</b>	$M_w$	$10^4 \sim 10^7$	<b>MALLS</b>
Sedimentation equilibrium method	$M_w$	$10^4 \sim 10^7$	ultracentrifugation
Viscometry	$M_v$	Wide range	viscometer
<b>Size exclusion chromatography (Gel permeation chromatography)</b>	$M_w, M_n$	Wide range	HPLC& UV or Differential refractometer

## 2. Synthetic Polymer chemistry ~classified into reaction type~

2-1. Chain polymerization(radicalic, anionic...etc)

2-2. Sequential polymerization(condensation, addition)

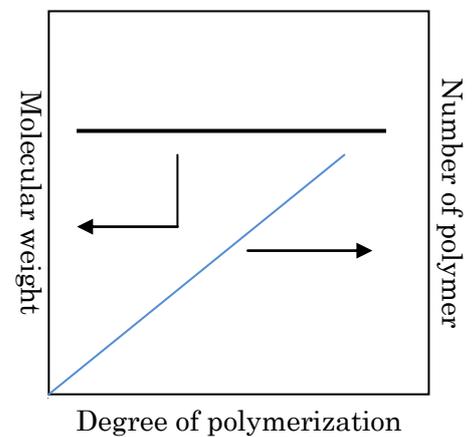
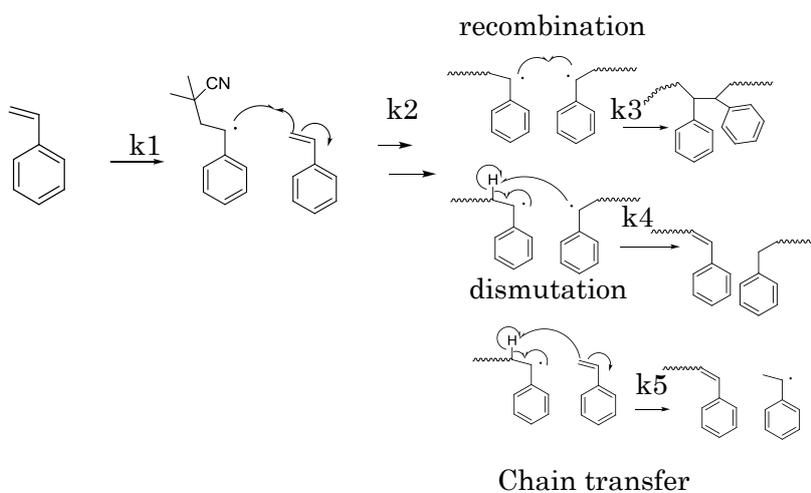
2-3. Living polymerization



### 2-1. Chain polymerization(radicalic, anionic...etc)

○Characteristic of reaction

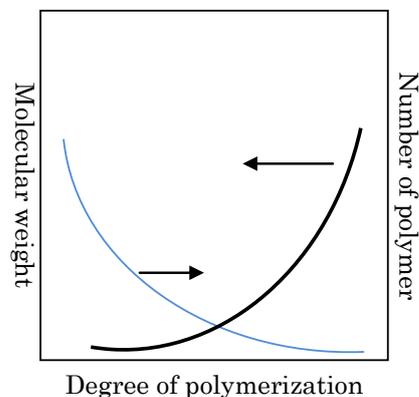
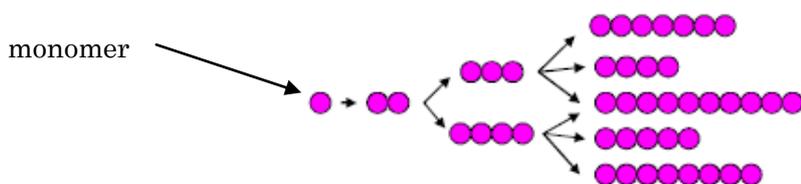
- Reactive species, such as radical or ion, are generated from the polymerization initiator.
- Reactive species react with monomers one after another to form a polymer.
- This reactive species is labile and disappears in a short time.
- Polymer growth reactions occur only with monomers and not between two polymers.
- High molecular weight polymers appear at the beginning.



## 2-2. Sequential polymerization(condensation, addition)

### ○Characteristic of reaction

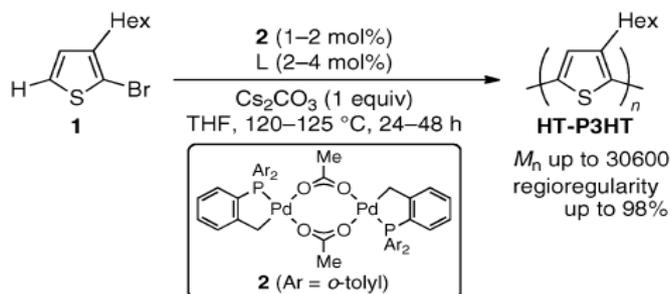
- Chain growth occur polymer-polymer or monomer-polymer.
- Condensation of monomer is rapidly decrease and monomer change oligomer
- Molecular weight gradually increase with reaction progress
- To get high degree of polymerization needs to excellent yield



### • Reaction Example

#### 1)Dehydrohalogenative polymerization

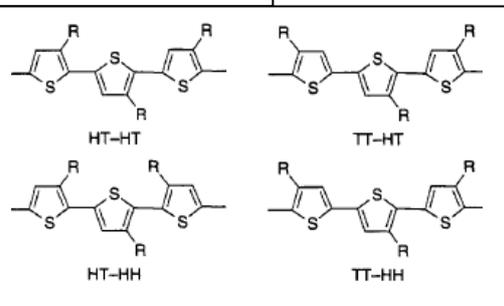
Ozawa, F, et al J. Am. Chem. Soc **2010**, *132*, 11420



HT: Head-to-tail

TT: Tail-to-tail

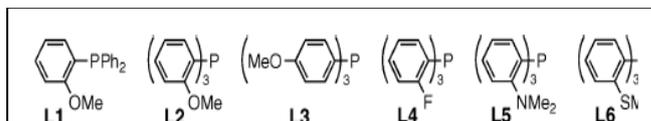
HH: Head-to-head



**Table 1.** Effect of Supporting Ligand (L) on Polycondensation of 1 Using 2 as the Catalyst Precursor<sup>a</sup>

entry	L <sup>b</sup>	HT-P3HT			
		M <sub>n</sub> <sup>c</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>	% HT <sup>d</sup>	yield (%)
1	P( <i>t</i> -Bu) <sub>3</sub>	1000	1.78	63	63
2	PCy <sub>3</sub>	900	1.76	64	58
3	PPh <sub>3</sub>	6200	2.53	77	53
4	L1	9900	2.16	89	99
5	L2	30300	2.42	93	99
6	L3	2400	2.04	68	99
7	P( <i>o</i> -tolyl) <sub>3</sub>	800	1.81	65	85
8	L4	1400	1.21	69	3
9	L5	24000	1.98	96	98
10 <sup>e</sup>	L5	30600	1.60	98	99
11	L6	1000	1.33	72	47

<sup>a</sup> Reactions were run at 120 °C for 48 h in THF (1 mL) using 1 (1 mmol), 2 (2 mol %), L (4 mol %), and Cs<sub>2</sub>CO<sub>3</sub> (1 mmol), unless otherwise noted. <sup>b</sup> The structures of L1–L6 are shown below. <sup>c</sup> Estimated by GPC calibration based on polystyrene standards. <sup>d</sup> Estimated by <sup>1</sup>H NMR spectroscopy. <sup>e</sup> The reaction was run at 125 °C for 24 h in THF (1 mL) using 1 (2 mmol), 2 (1 mol %), L5 (2 mol %), and Cs<sub>2</sub>CO<sub>3</sub> (2 mmol).



Rieke, R, D et al

J. Am. Chem. Soc. **1995**, *117*, 233

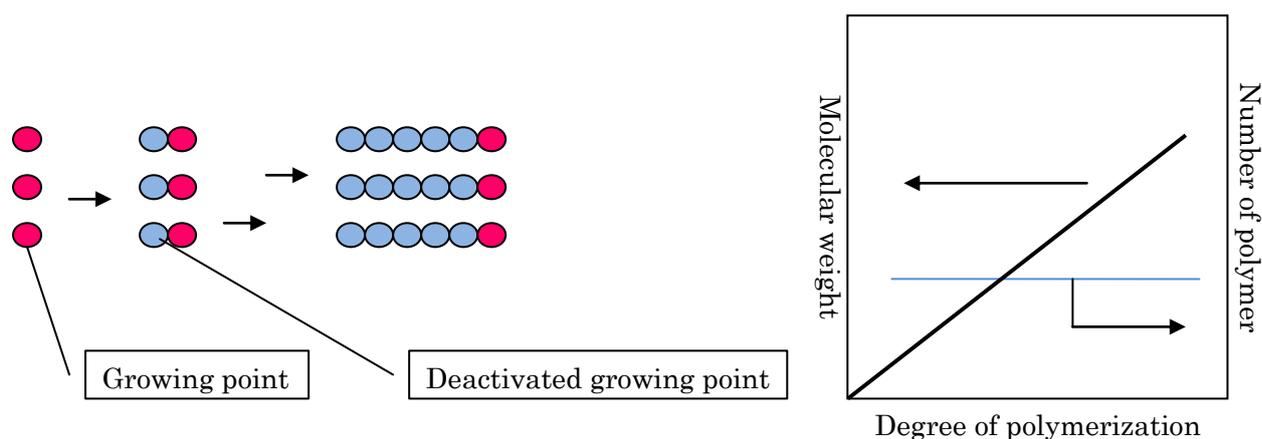
The catalytic performance is dependent on the supporting ligand.

According to table1

- Electronic-effect contribute to yield.
- Coordinating substituents in phenyl group act good regio-regularity.

## 2-3. Living polymerization

- chain-growth polymerization that propagates with no irreversible chain-transfer or chain-termination reactions .
- degree of polymerization is proportional to the ratio of the concentrations of monomer consumed and initiator
- Providing the narrowest MW distribution polymer(MW distribution =  $M_w/M_n$ ).
- The growing point at polymer terminal is always a polymerization activity. (= living)
- If monomer is completely consumed, new added monomer reacts with living polymer



## • Reaction Example

### 1. Living polymerization with titanium complex

Fujita, T et al Angew. Chem. Int. Ed. 2001. 40. 2918

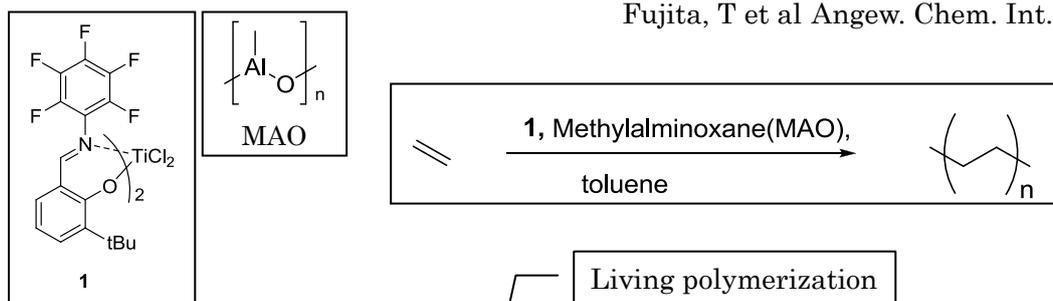


Table 1. Results of ethylene polymerization using complex **1**,  $[\text{Cp}_2\text{ZrCl}_2]$ , or  $[\text{Cp}_2\text{TiCl}_2]$ .<sup>[a]</sup>

Entry	Complex	Yield [g]	TOF $[\text{min}^{-1}\text{atm}^{-1}]$	$M_n$ $[\times 10^3]$	$M_w/M_n$	$T_m$ $[\text{°C}]$
1	<b>1</b>	0.28	20000	412	1.13	135.2
2	$[\text{Cp}_2\text{ZrCl}_2]$	0.26	18600	157	1.73	133.4
3	$[\text{Cp}_2\text{TiCl}_2]$	0.43	30500	309	1.97	134.9

[a] Conditions: ethylene, atmospheric pressure ( $1667 \text{ mL}\cdot\text{min}^{-1}$ ), toluene (250 mL), 25 °C, 1.0 min, catalyst (0.5  $\mu\text{mol}$ ), cocatalyst MAO (125 mmol, purchased from Albemarle).

Table 2. Results of ethylene polymerization with complex **1** using ethylene-saturated toluene under  $\text{N}_2$  or  $\text{N}_2$  followed by ethylene feed.<sup>[a]</sup>

Entry	Conditions	Yield [g]	$M_n$ $[\times 10^3]$	$M_w/M_n$
1	5 min under $\text{N}_2$	0.800	65.8	1.10
2	35 min under $\text{N}_2$	0.775	73.0	1.12
3	1. 35 min under $\text{N}_2$ 2. 2 min with ethylene <sup>[b]</sup>	1.317	98.6	1.17

[a] Conditions: toluene (250 mL, saturated with ethylene), complex (**1**) (10  $\mu\text{mol}$ ), cocatalyst MAO (2.5 mmol). [b] Ethylene ( $333 \text{ mL}\cdot\text{min}^{-1}$ ).

$[\text{Cp}_2\text{TiCl}_2]$  produced polyethylenes having an  $M_w/M_n$  value of 3.31-3.45 under the conditions, indicating that  $\text{Cp}_2\text{TiCl}_2$  under these conditions

Table 3. Results of ethylene polymerization with complex **1** at various temperatures<sup>[a]</sup>

Entry	<b>1</b> [ $\mu\text{mol}$ ]	$T$ [ $^\circ\text{C}$ ]	$t$ [min]	Yield [g]	TOF [ $\text{min}^{-1}\text{atm}^{-1}$ ]	$M_n$ [ $\times 10^3$ ]	$M_w/M_n$
1	0.5	50	0.5	0.17	24300	257	1.08
2	0.5	50	1.0	0.30	21400	424	1.13
3	1.0	75	0.5	0.25	17900	214	1.09
4	1.0	75	1.0	0.45	16100	329	1.15
5	2.0	90	0.5	0.20	7140	102	1.22
6	2.0	90	1.0	0.46	8210	167	1.30

[a] Conditions: ethylene, atmospheric pressure ( $1667\text{ mL min}^{-1}$ ), toluene ( $250\text{ mL}$ ), cocatalyst MAO ( $1.25\text{ mmol}$ , purchased from Albemarle).

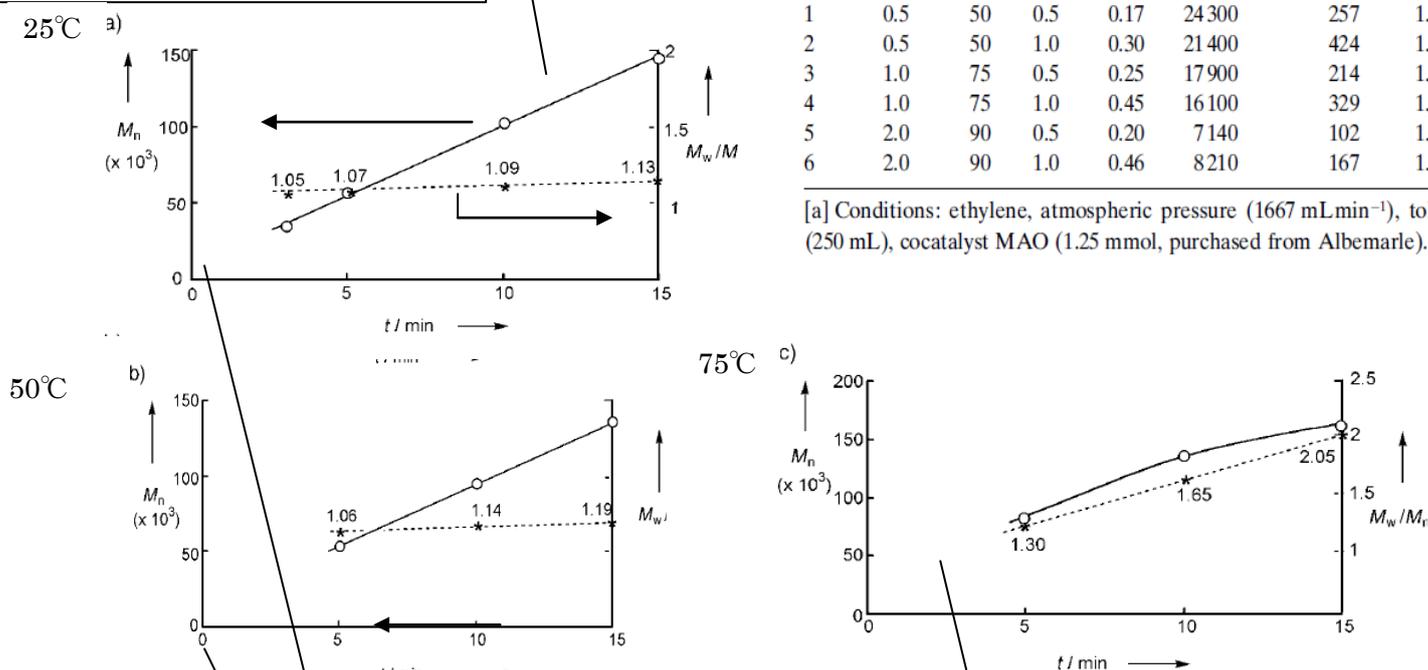


Figure 2. Plots of  $M_n$  and  $M_w/M_n$  as a function of polymerization time  $t$  for ethylene polymerization at a)  $25^\circ\text{C}$ , b)  $50^\circ\text{C}$ , and c)  $75^\circ\text{C}$  using diluted ethylene ( $33\text{ mL h}^{-1}$  for a, b;  $83\text{ mL h}^{-1}$  for c) with nitrogen ( $833\text{ mL h}^{-1}$ ; **1**:  $1\ \mu\text{mol}$ , MAO:  $1.25\text{ mmol}$ ).  $\circ$ :  $M_n$ ,  $*$ :  $M_w/M_n$ .

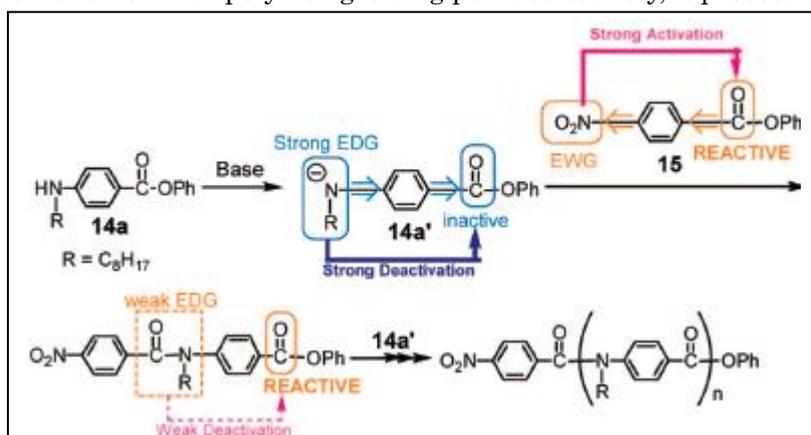
A linear relationship between  $M_n$  and polymerization time as well as a narrow range of  $M_w/M_n$  values were found for all runs, indicating a living polymerization

At  $75^\circ\text{C}$ , chain termination or transfer maybe occurred, but still possessed some characteristics of living polymerization

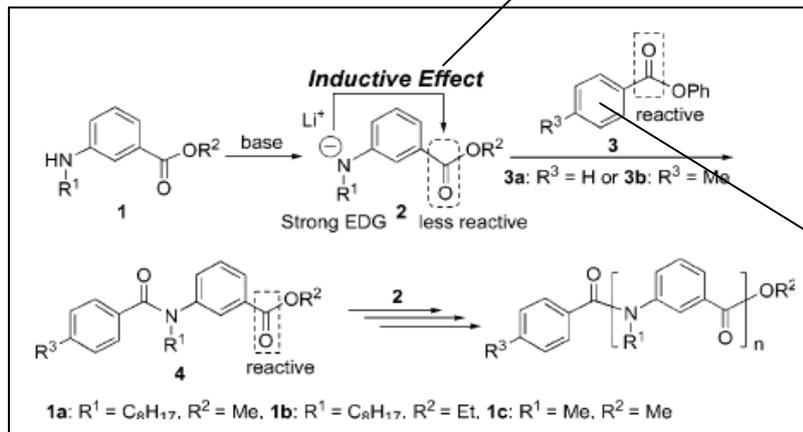
## 2) Living polymerization condensation

Yokozawa, T and Yokoyama, A Chem. Rev. Soc **2009**, *109*, 5595

As for condensation polymerization, the monomer has reactive group at both tail. It induce reaction with monomer to monomer at beginning. Afterward, oligomer or monomer reacts with either in disorder. (It is to say sequential polymerization). For the above mentioned reason, poly condensation cannot be living polymerization intrinsically. However, if it can inhibit monomer homo coupling and react monomer with polymer-growing point selectively, it proceed chain polymerization.



N-terminal is activated and carbonyl group is deactivated. (It is to say, homo coupling doesn't occur)



Polymerization initiator

**Table 1.** Polymerization of **1** with **3**<sup>a</sup>

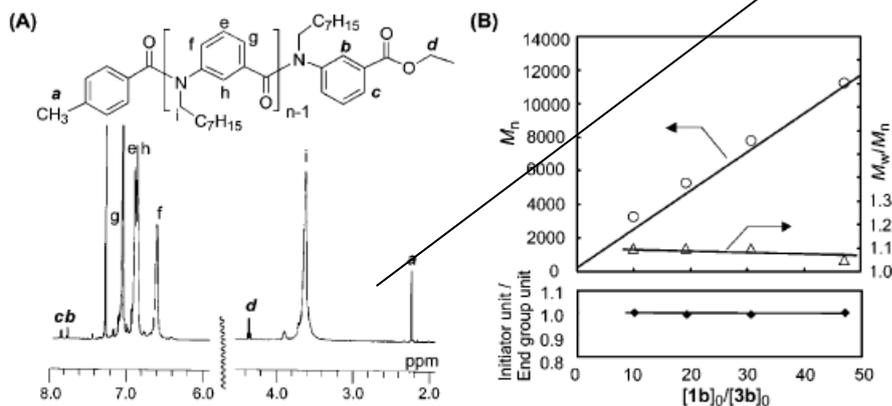
entry	<b>1</b>	<b>3</b>	base	T (°C)	[ <b>1</b> ] <sub>0</sub> /[ <b>3</b> ] <sub>0</sub>	time	conv. <sup>d</sup> (%)	M <sub>n</sub> calcd	M <sub>n</sub> <sup>e</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>e</sup>
1	1a	3a	LDA	-78	19.6	8 h	85	3990	3940	1.24
2			LiTMP <sup>b</sup>	19.3	19.3	5 h	74	3540	2820	1.11
3			LiN( <i>i</i> -Pr) <sup>c</sup> Bu	18.9	18.9	5 h	87	3780	3250	1.09
4			LiHMDS <sup>c</sup>	19.1	19.1	5 h	98	4100	3700	1.08
5			LiHMDS	34.5	34.5	6 h	96	7750	4560	1.10
6			LiHMDS	-30	39.8	1 h	96	8930	7210	1.12
7			LiHMDS	0	47.3	5 min	98	10800	9690	1.18
						1 h	98		9790	1.25
8	1b	3b	LiHMDS	0	47.1	5 min	100	10800	10000	1.05
						2 h	100		10000	1.05

Molecular weight dispersity is very small

[**1**]<sub>0</sub> ratio relative to MW

<sup>a</sup> Polymerization of **1** with **3** in the presence of 1.1 equiv of base in THF ([**1**]<sub>0</sub> = 0.40 M). <sup>b</sup> Lithium 2,2,6,6-tetramethylpiperidide. <sup>c</sup> Lithium hexamethyldisilazide. <sup>d</sup> Determined by GC. <sup>e</sup> Determined by GPC based on polystyrene standards (eluent: THF).

The integral ratio a:b:c:d=3:1:1:2



**Figure 1.** (A) <sup>1</sup>H NMR spectrum of poly**1b** obtained by the polymerization of **1b** with **3b** in the presence of 1.1 equiv of LiHMDS in THF at 0 °C. (B) M<sub>n</sub> and M<sub>w</sub>/M<sub>n</sub> values of poly**1b**, obtained with 1.1 equiv of LiHMDS in the presence of **3b** in THF ([**1b**]<sub>0</sub> = 0.40 M) at 0 °C, as a function of the feed ratio of **1b** to **3b**. The lines indicate the calculated M<sub>n</sub> values assuming that one polymer chain forms per unit of **3b**.

### 3. Reversible polymers for Smart polymer

#### 3-1: Introduction

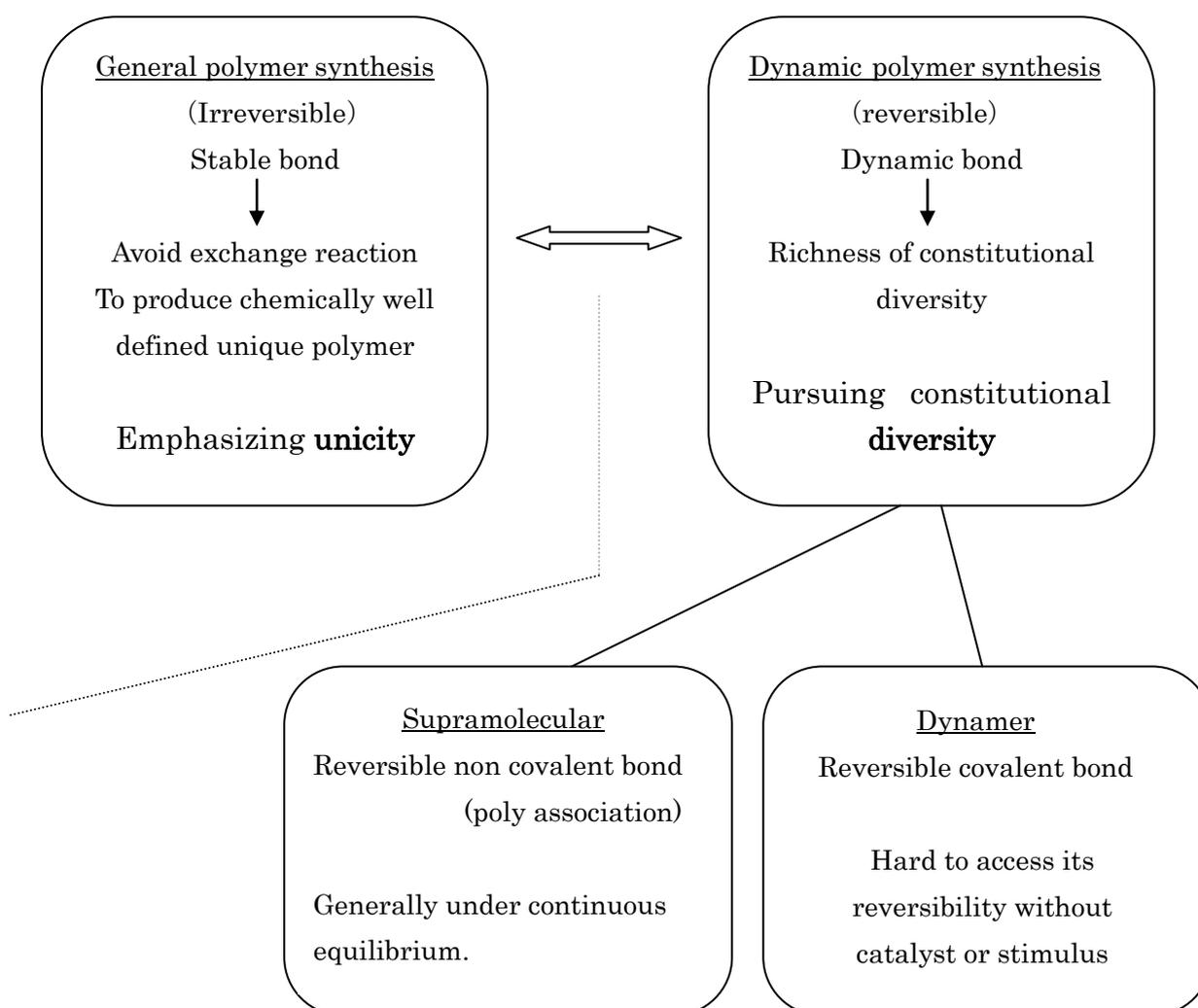
• The development of the above-mentioned reaction lead investigation into polymer with various physical properties.

One of them is adaptive/stimuli-responsive polymer

(= Smart polymer)

• Smart polymer is composed by supramolecular ( non-covalentbond) or Dynamer (covalent bind) . This time, I intend to introduce example of Dynamer

○Compared with General polymer synthesis standpoint



Lehn, J. -M. et al, Proc. Natl. Acad. Sci.USA **2004**, *101*, 8270

Lehn, J. -M. et al, Prog. Polym. Sci. **2005** *30*, 814

Lehn, J. -M. et al, Chem. Soc. Rev. **2007**, *36*, 151

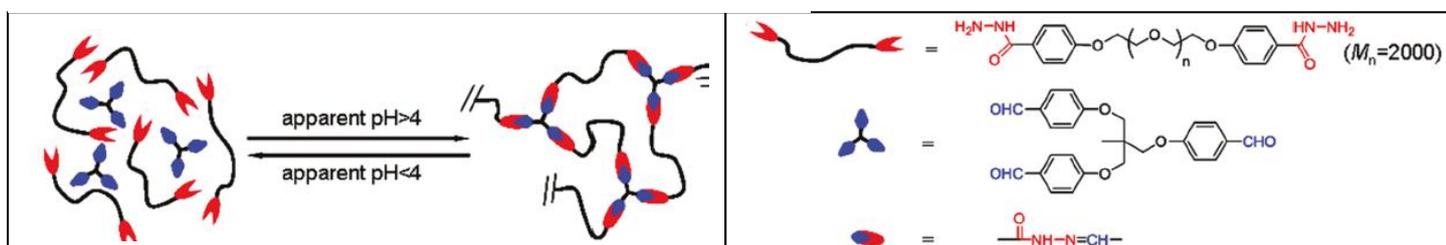
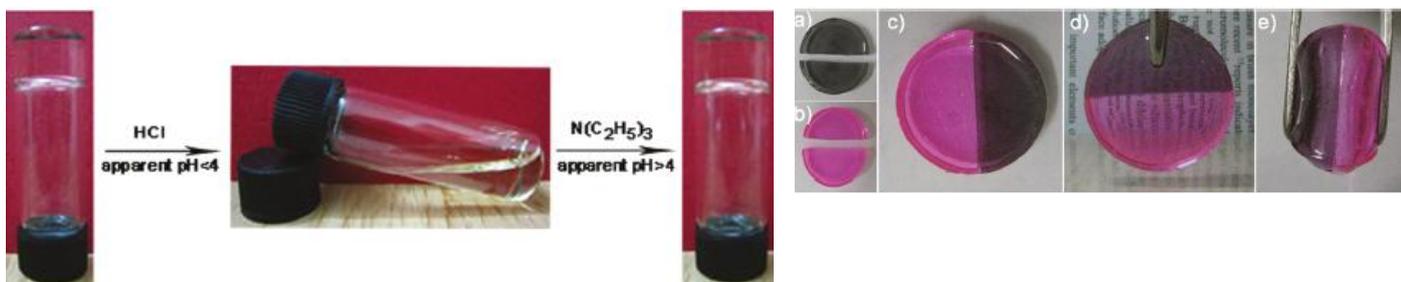
Rowan, S. J et al, Nature mater **2010**, *10*, 14

### 3-2. pH responsive smart polymer

#### ○ Polymer Gels with Reversible Sol-Gel Transition and Self-Healing Properties

Chen, Y. et al Macromolecules, 2010, 43, 1191

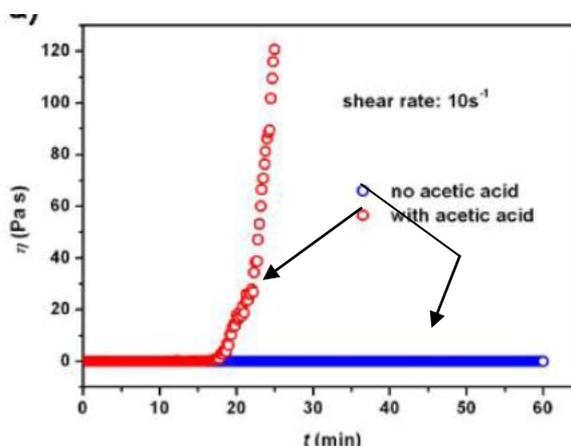
<Picture of sol-gel transition and Self-Healing properties.>



Acidic catalyst (it give around ph 6) is necessary for the gelation because acylhydrazone formation is very slow at neutral conditions while a catalytic amount of acid drastically accelerated the reaction

#### • Gel forming

Predetermined amount of bis-acylhydrazone functionalized PEO polymer (**A2**) and equivalent tris[4-formylphenoxy] methyl]ethane (**B3**) were mixed in a certain amount of DMF to form a homogeneous solution in a container. After catalyst of acetic acid was added and mixed homogeneously, the solution was sealed in the container and placed at ambient temperature without stirring until a gel was formed.

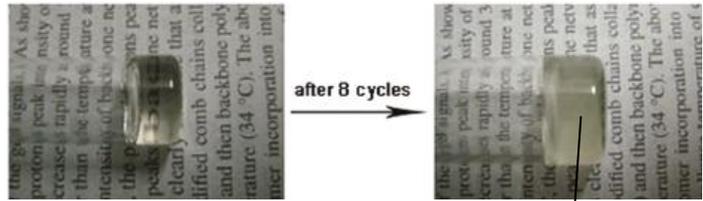


Viscosity ( $\eta$ ) change vs. time during gelating process of mixture A2 and B3 in DMF (gelator concentration 12 wt %) at 25°C. blue circle: no acetic acid was added; red circle: glacial acetic(apparent ph =  $\sim 5$ )

• Sol-gel phase transition ability in response to acidity change

The gel used was prepared in 0.5 mL DMF with gelator concentration 12 wt % and acetic acid concentration 15% v/v (apparent pH ~5). After the gel aged overnight, 5µL of hydrochloric acid (~37%) was added on the gel surface.

The gel completely decomposed into a sol in 1.5 h with a final apparent pH 3-4. When 8 µL triethylamine (equivalent to hydrochloric acid) was added, the sol transformed into the gel in 20 second.



Appearance of the original gel (left) and the gel after eight transition cycles (right).

During the repeated transition cycles, white salts of HCl and triethylamine gradually appeared due to its low solubility in DME

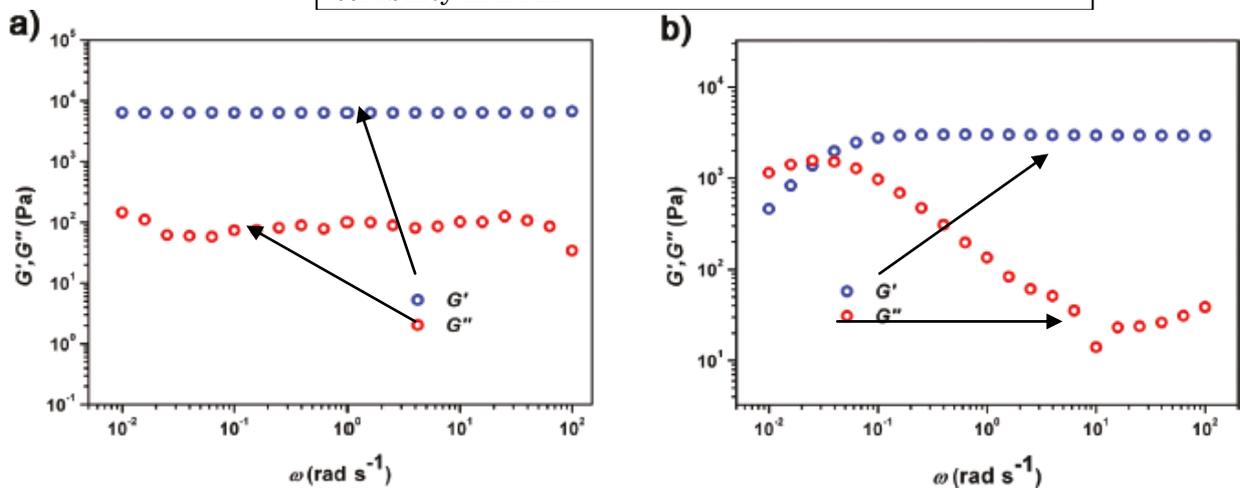
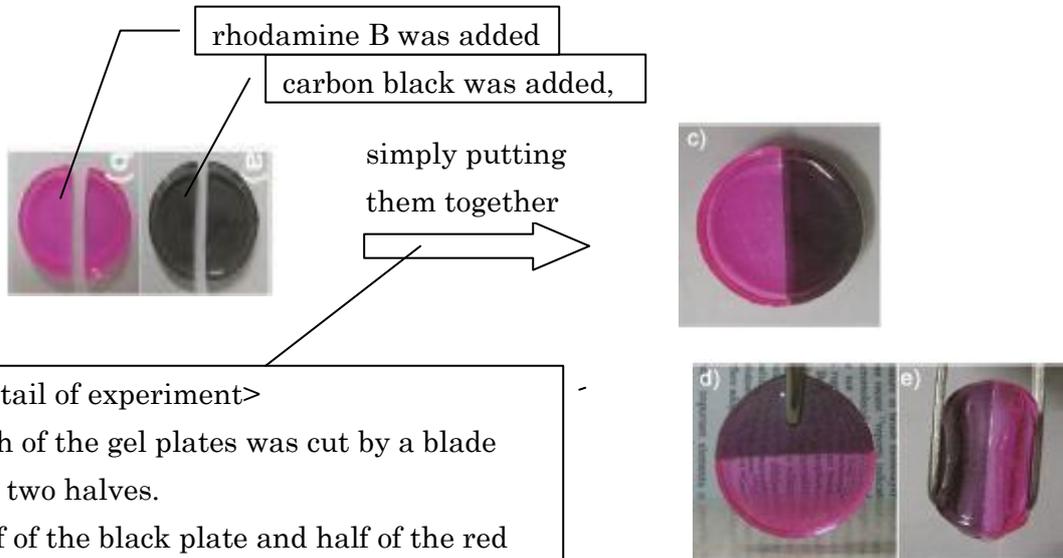


Figure 1. (a) Storage modulus ( $G'$ ) and loss modulus ( $G''$ ) vs angular frequency ( $\omega$ ) of the polymer gel (gelator concentration 12 wt %, acetic acid concentration 15% v/v) at 25°C after aging 17 h; (b) storage modulus ( $G'$ ) and loss modulus ( $G''$ ) vs angular frequency ( $\omega$ ) of the gel after three sol-gel transition cycles.

• Self-Healing

Polymer gel plates



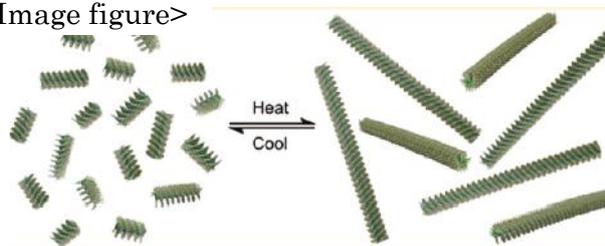
<Detail of experiment>  
 Each of the gel plates was cut by a blade into two halves.  
 Half of the black plate and half of the red plate were spliced in the original round bottle by simply putting them together and keeping contact

### 3-3. Thermo responsive smart polymer

#### ○Thermally Induced, Reversible Chain Elongation of Amphiphilic Poly (acylhydrazones)

Lehn, J. -M. et al J. Am.Chem. Soc. 2011. 133. 10966

<Image figure>



<Reaction>

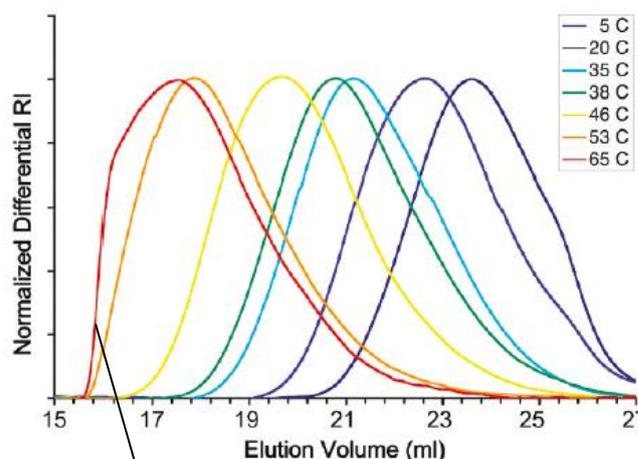
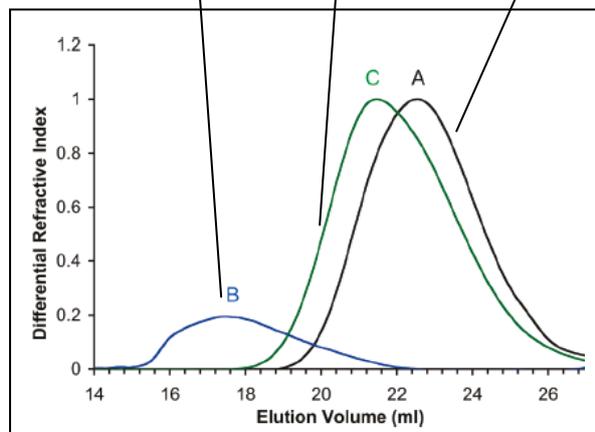
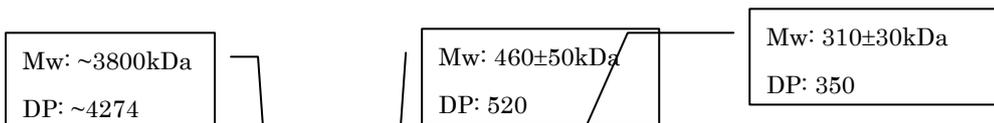
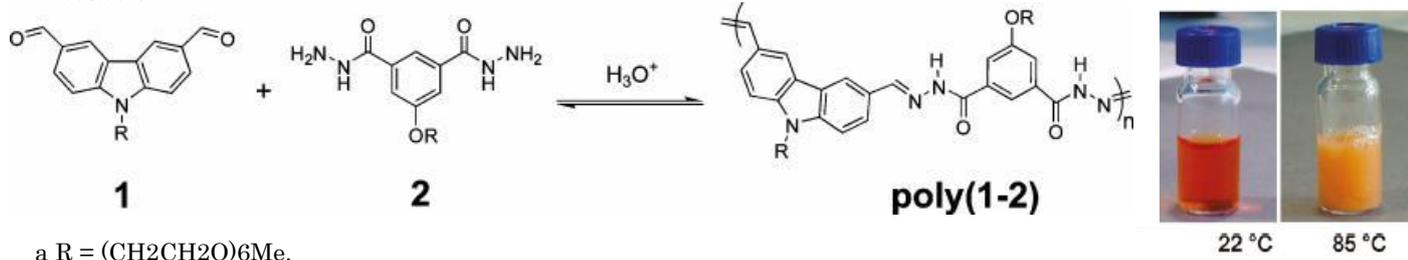


Figure 2. Size exclusion chromatography (SEC) traces of a sample of poly(1–2) prepared by mixing 1 (6.1 mM) and 2 (5.9 mM) in water at pH 2.0 for 48 h (black trace,  $M_w = 310 \pm 30$  kDa), immediately after heating the sample above the lower critical solution temperature (to 80 °C) for 4 h (blue trace,  $M_w \sim 3800$  kDa) and after allowing the sample to cool to room temperature and stand for 20 h (green trace,  $M_w = 460 \pm 50$  kDa). A poor correlation between calculated and injected masses prohibits an accurate determination of the high  $M_w$  sample (blue trace).  $M_w$  values determined by multiangle laser light scattering (MALLS).

Figure 3. Size exclusion chromatography traces of aqueous solutions of poly(1–2) ( $[1]_0 = [2]_0 = 550 \mu\text{M}$ , pH = 1.8) equilibrated for 3 days at different temperatures.

Too large for accurate analysis

Fig3 shows effect on Mw, the more Temperature is higher the more Mw is higher

Fig.2 shows Mw changing in reaction cycle, A,C that are under r,t, are lower Mw and B is higher Mw

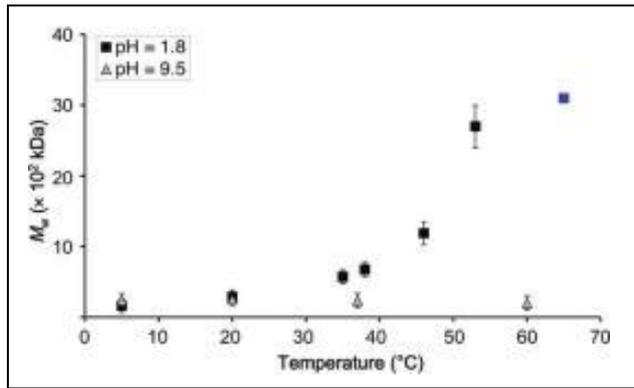


Figure 4. Weight-averaged molecular weight ( $M_w$ ) determined by SEC/MALLS as a function of temperature for samples of poly(1–2) from Figure 3, as well as identical control samples, adjusted to pH 9.5 prior to temperature adjustment. The  $M_w$  of the 65 °C sample (blue square) is too large to be determined accurately and therefore represents a crude estimate.

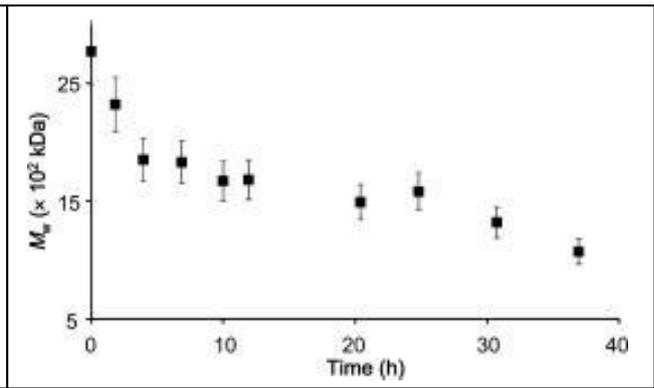


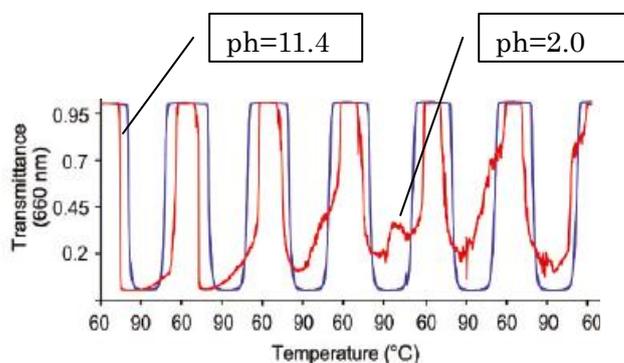
Figure 5. Weight-averaged molecular weight ( $M_w$ ) determined by SEC-MALLS as a function of time after cooling a sample of poly(1–2) which had equilibrated for 3 days at 55 °C to ambient temperature.

~Why this component can be polymerize under heating condition (Generally polymer is decomposed under heating condition. e.g. cyclopentadiene)~

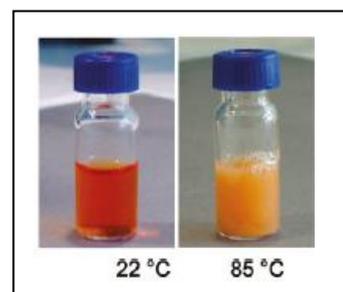
### 1) Utilization of LCST

- Polyethylene oxide(PEO) have LCST.

(LCST(Lower critical solution temperature) = Critical temperature below which a mixture is miscible.)



Turbidity diagrams at 660 nm for aqueous solutions of poly(1\_2) ([1]<sub>0</sub> = [2]<sub>0</sub> = 1.0 mM) under acidic and basic conditions as a function of heat/cool cycles (rate = 1 °C/s).



⇒ LCST can make partial higher concentration suddenly by aggregation.

## Molecular dynamic simulation

**TABLE 1: Excess Thermodynamic Quantities for DME Solutions**

$T$ (K)	$N_{ew}^b$	$\Delta G^{EX}$ (kcal/mol)	$\Delta H^{EX}$ (kcal/mol)	$\Delta S^{EX}$ (kcal/(mol K))	$-T\Delta S^{EX}$ (kcal/mol)
$w_p = 0.01$					
298 <sup>a</sup>	1.54	-6.2	-17.1	-0.037	10.9
363	1.41	-3.5	-14.0	-0.029	10.5
$w_p = 0.52$					
298	1.13	-4.0	-9.8	-0.019	5.8
363	0.92	-3.0	-8.2	-0.015	5.3
$w_p = 0.01$ without Ether-Water Hydrogen Bonding					
298 <sup>b</sup>	0.13	-2.4	-12.2	-0.033	9.9
363	0.15	-1.1	-7.2	-0.017	6.3

<sup>a</sup> From ref 8. <sup>b</sup> Number of ether-water hydrogen bonds per ether oxygen, defined in ref 8.

$w_p$ : weight fraction of ether in the solution

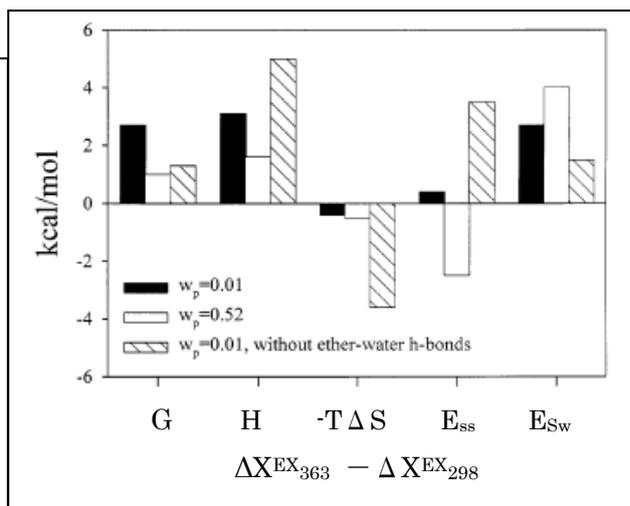
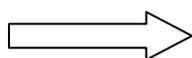


Figure 2. Temperature dependence of excess thermodynamic properties of DME/water solutions

Bedrov, D et al *J. Phys. Chem. B*, **2003**, *107*, 3095



LCST in PEO/water solutions is enthalpy-driven

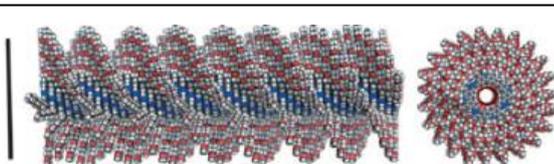
## 2) Stabilization with helical conformation

- This polymer grows with the formation of large bundles of intertwined rods as observed by TEM
- The folded aromatic backbone is thought to shield the acylhydrazone linkages from bulk solution

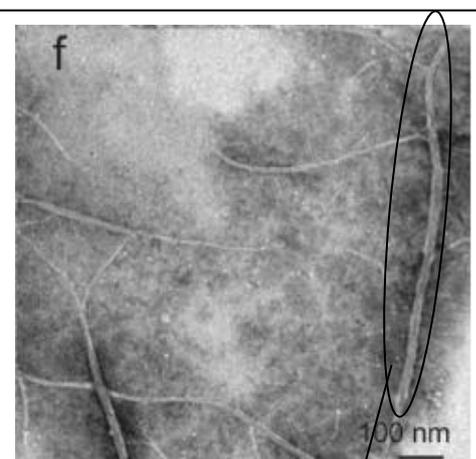
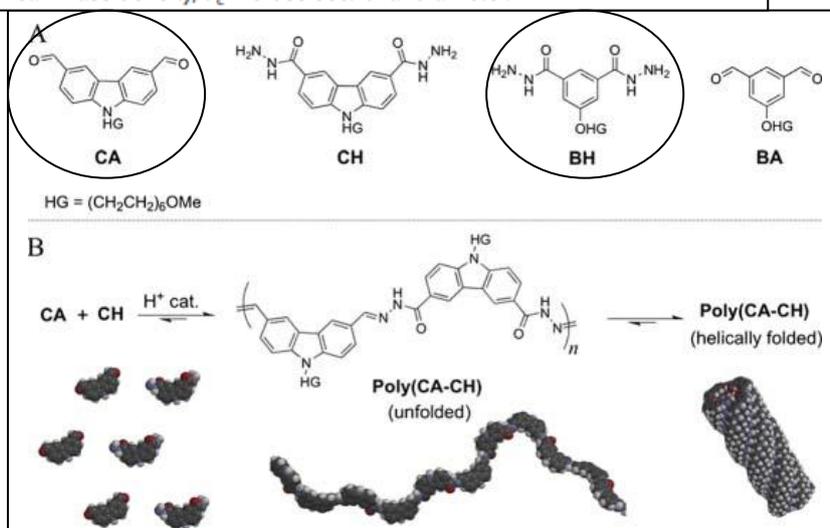
**Table 1: Physical dimensions of rodlike polymers as determined by fitting of SANS data.<sup>[a]</sup>**

Sample	$M_w$ [kDa]	$R_g$ [nm]	$\mu$ [kDa nm <sup>-1</sup> ]	$d_c$ [nm]
poly(BA-CH)	340 ± 40	11 ± 2	8.4 ± 10	4.4 ± 0.3
poly(CA-CH)	280 ± 30	10 ± 2	7.5 ± 9	4.4 ± 0.3
poly(BA-BH)	140 ± 20	6 ± 2	6.7 ± 8	4.1 ± 0.3
poly(CA-BH)	200 ± 20	8 ± 2	6.6 ± 8	4.4 ± 0.3

[a]  $M_w$  = weight-averaged molecular weight,  $R_g$  = radius of gyration,  $\mu$  = linear mass density,  $d_c$  = cross-sectional diameter.



*Angew. Chem. Int. Ed.* **2009**, *48*, 7664



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Helical folded tube

Lehn, J.-M. et al *Polym. Int.* **2010**, *59*, 1477

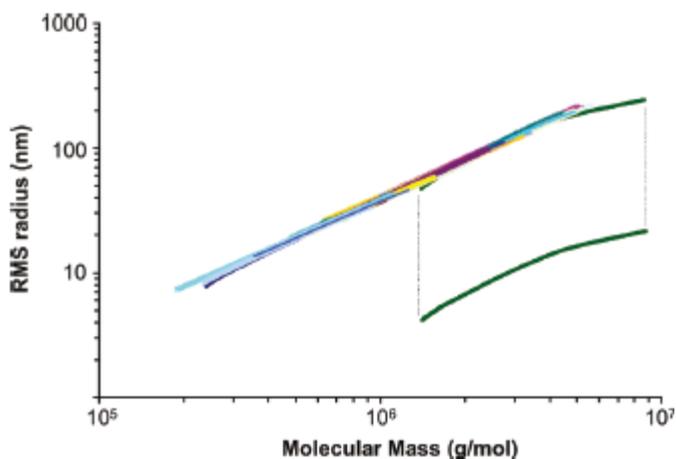


Figure 6. Radius of gyration vs molecular mass relationships determined by MALLS analysis of SEC fractions for samples from Figures 2, 4, and 5. A linear relationship is indicative of rodlike objects,<sup>30</sup> and the slope is related to the linear density of the rods. The nonlinear green curve corresponds to the high  $M_w$  sample from Figure 2 and has been offset for clarity.

~Summary~

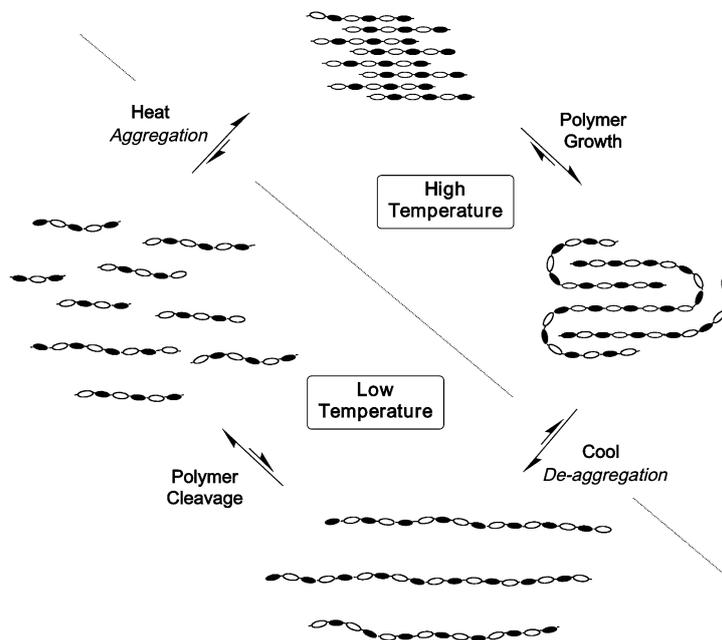
Di(aldehyde) **1** and Di(acylhydrazine) **2**  
make thermodynamic polymer in acidic condition.

Growing condition)

- High temperature.
- Driving force=aggregation (LCST)and making helical folded tube.

Decomposition condition)

- Low temperature
- Driving force=deaggregation and easier to interact with bulk solution.

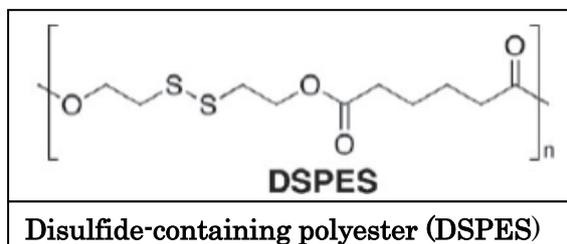


This polymer is expected to apply hyperthermic drug delivery chemo-mechanical device ...etc

### 3-3. Photo responsive smart polymer

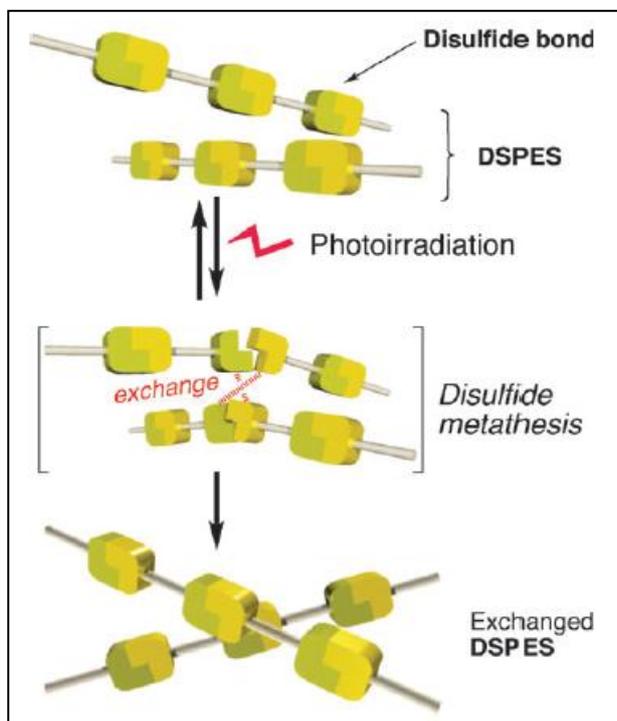
A dynamic covalent polymer film driven by disulfide metathesis under photo irradiation.

Otuka, H et al, Chem. commun, 2010, 46, 1150



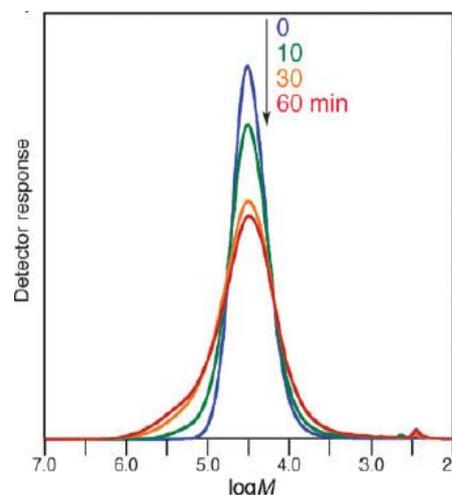
Polymer film image  
(...not made of this polymer)

Method: Drop casting technique:  
The solution pour to glass board kept level and wait until solvent disappear



Expeliment 1: Confident the exchange reaction of disulfide bond between the main chain

The film of fractionated DSPES [ $M_n=12\ 000, M_w/M_n=1.21$ ] was photoirradiated in hexane at 30 °C under an argon atmosphere. Although the NMR spectrum did not change, the GPC profiles drastically changed after photoirradiation for 60 min



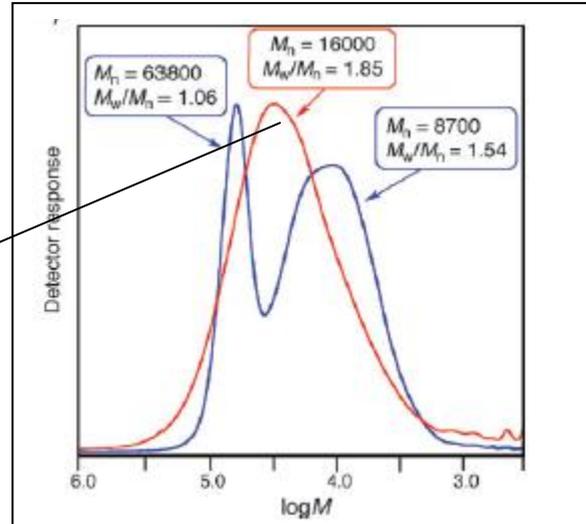
SEC profiles of DSPES exposed to UV light for 0 min (blue line), 10 min (green line), 30 min (orange line), and 60 min

Experiment 2 : To demonstrate the re-organizability

The polymer films, consisting of equal quantities of h-DSPES ( $M_n = 60\,400$ ,  $M_w/M_n = 1.06$ ) and l-DSPES ( $M_n = 8700$ ,  $M_w/M_n = 1.54$ ) that showed two apparent peaks in the GPC profile, were photoirradiated under the same conditions.

After 60 min, the peaks derived from h-DSPES and l-DSPES clearly fused into a unimodal peak,

Two peaks are integrated one peak ( $M_n = 16,000$ )



Scheme 1 Macromolecular crossover reaction of disulfide-containing polyester (DSPES) driven by disulfide metathesis under photoirradiation.

**4. Summery**

- The polymer material is widely used for all food, clothing, and housing regardless of nature and artificial.
  - ↓
  - The development of a new polymer synthesis method and the development of functional polymer are very important.
- Polymer synthesis can be classified into three reaction type.
  - The narrowest molecular weight dispersity is Living polymerization (= the most controlled polymerization) but cannot be controlled satisfactorily still.
- Smart polymer = dynamic character can be accessed when specific external factors are exist.
  - ↓
  - {
    - Adaptable reaction is still few
    - Difficult to take balance of reaction condition with reaction time
  - ↓
  - It is possible to provide for the application to drug delivery and stimulus-mendable polymeric material, etc. in the future.