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Carbon Materials for Today and Future
Turkish-Japanese Joint Carbon Symposium
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Pyrolytic Conversion of Structured Polymeric Materials to Porous Carbons

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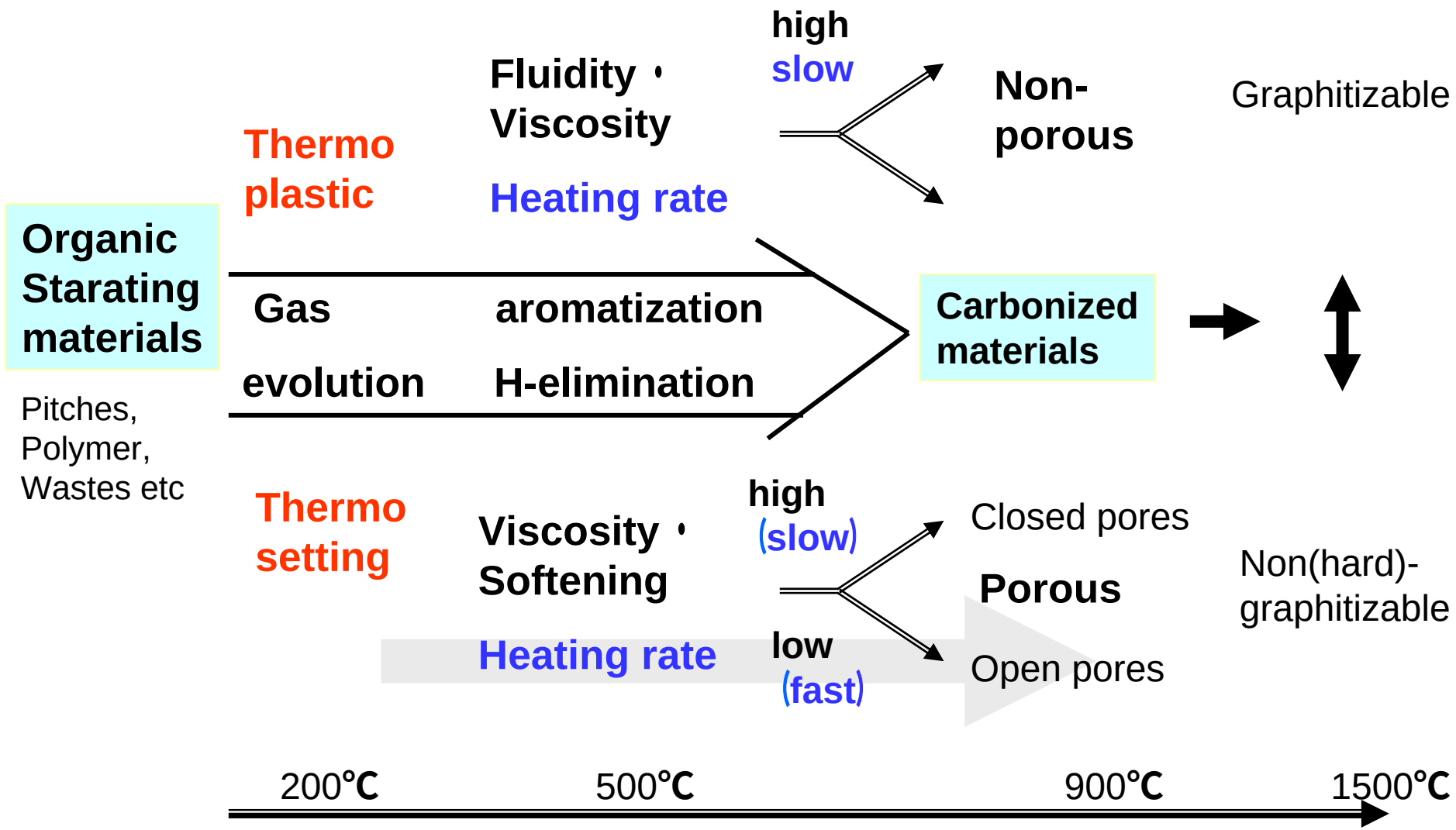
Carbonization process of organic materials



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Approaches to prepare porous carbons by pyrolytic methods

- From poly(*m*-phenylenebutadiynylene)s, P*m*PB, a rigid conjugated polymer

- From lignin-cellulose composites, wooden biomass materials

- From synthetic organic zeolites:

  Coordination polymers = Metal organic frameworks (MOFs) , Covalent organic frameworks (COFs), and microporous polymers

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(1) Pyrolytic conversion of structured poly(*m*-phenylenebutadiynylene)s P*m*PBs to porous C

(2) Pyrolytic conversion of structured Lignin-Cellulose composites to porous C

(3) Pyrolytic conversion of MOFs and COFs to porous C

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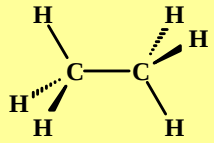
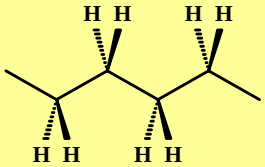
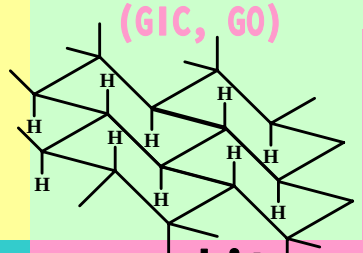
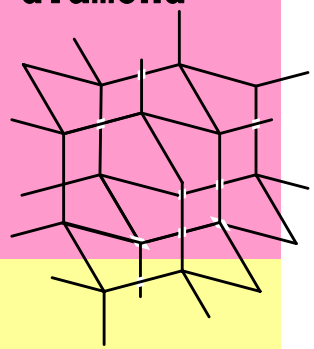
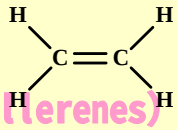
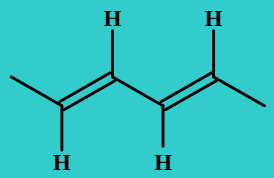
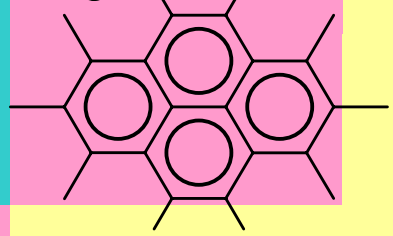
Classification of C−C bonded materials having different hybrid orbitals and dimensions

hybrid orbital	dimension 0	1	2	3
sp^3	ethane 	polyethylene 	Polymethyne (GIC, GO) 	diamond 
sp^2	ethene  (fullerenes)	polyacetylene 	graphite 	
sp	ethyne  (Cyclocarbons)	polyethynylene —C≡C—C≡C— ═C═C═C═C═ (carbyne)		

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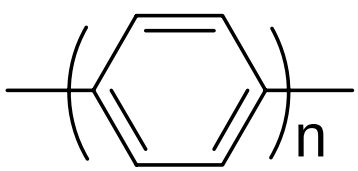
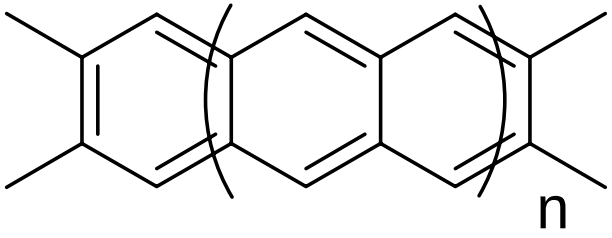
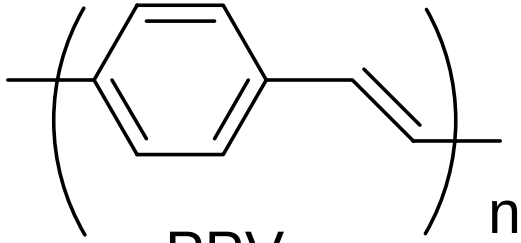
Some conjugated polymeric materials for preparation of carbon materials



PPP

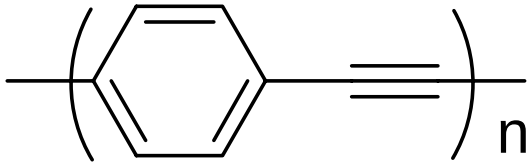


polyacene



PPV

Good starting materials for Carbons



PPE

PPB

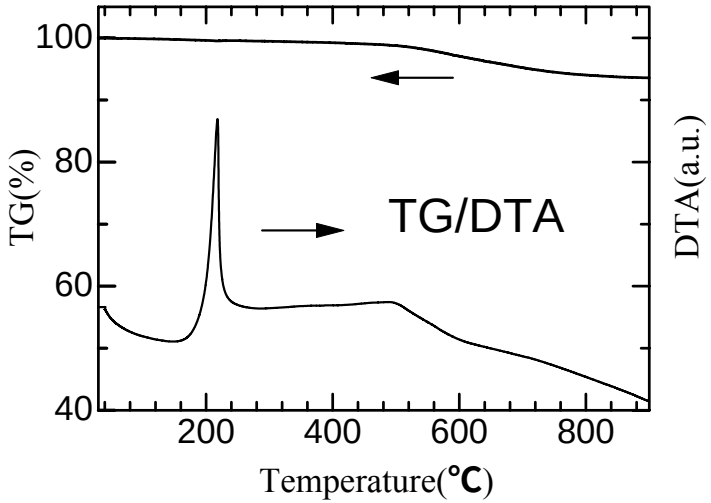
High content of C **High yield carbonization behavior (>90% yield)**

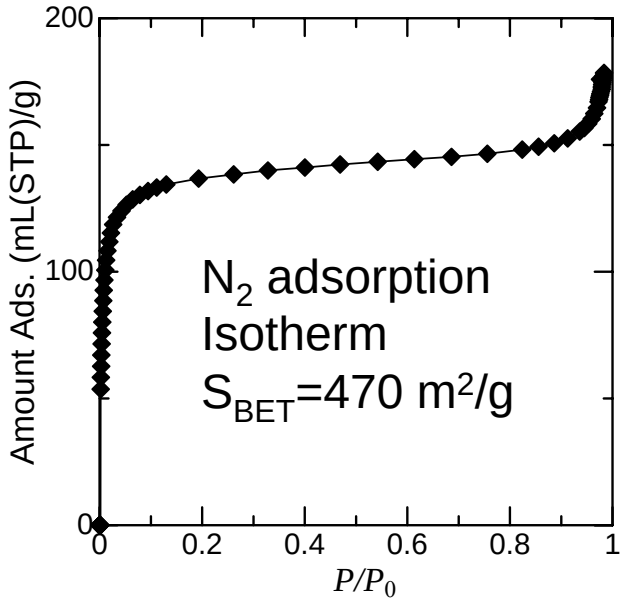
To prepare one of the models of amorphous C

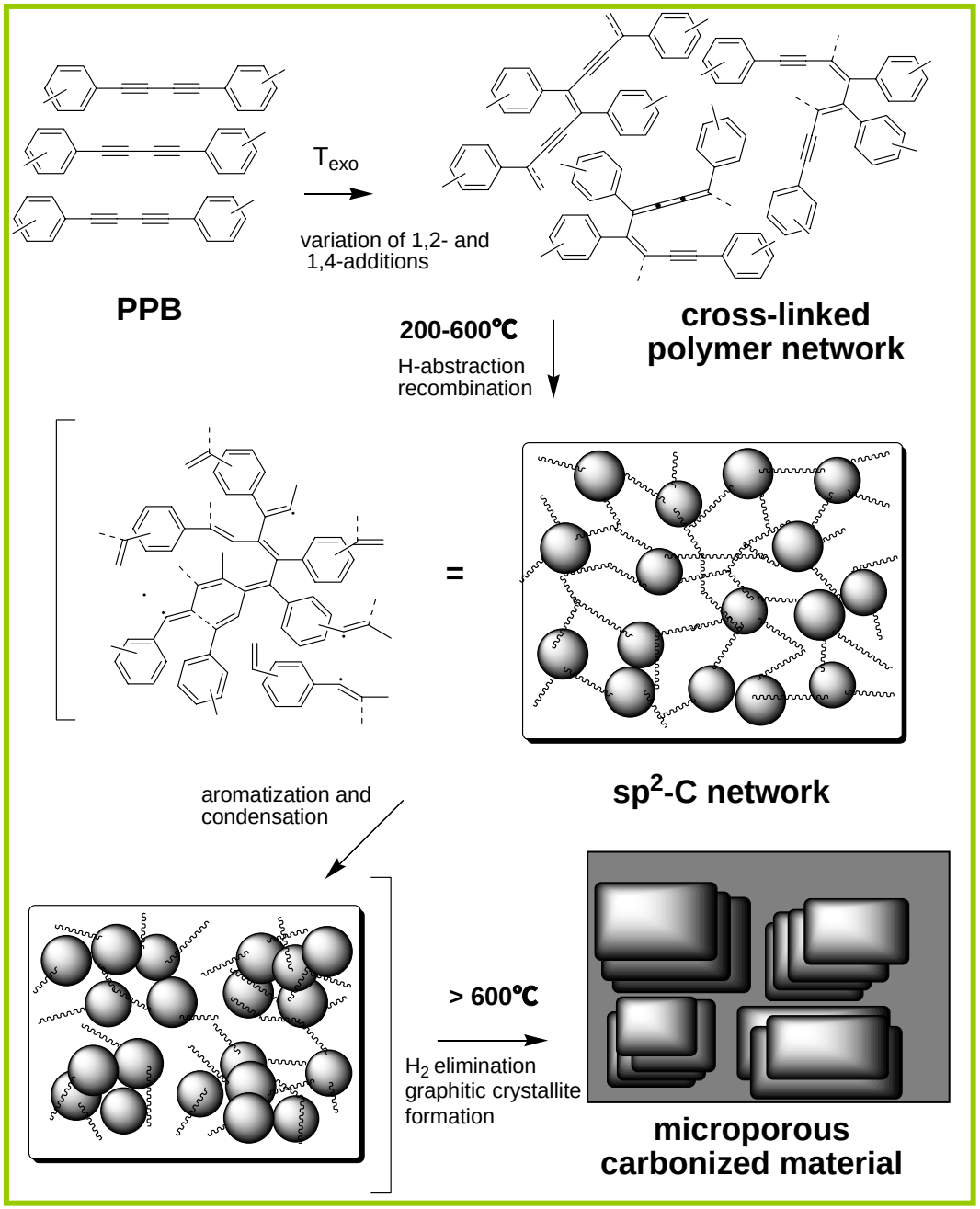
E. Fitzer et al., *High Temp. High Press.*, **3** (1971) 53.

A. E. Newkirk, et al., *J. Polym.Sci., Part A*, **2** (1964) 2217.

Thermal conversion of P*m*PB to microporous carbons in high yield







M. Kijima et al., Carbon, 45(2007) 594-601

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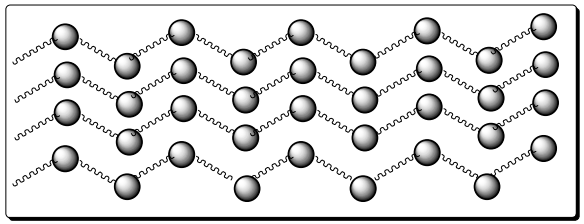
Pyrolytic conversion of structured poly(*m*-phenylenebutadiynylene)s **P*m*PBs** to porous C

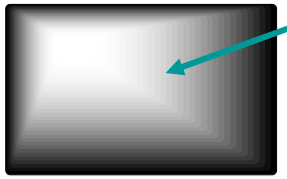


Polymer blocks

Rigid backbone

→

strong interaction



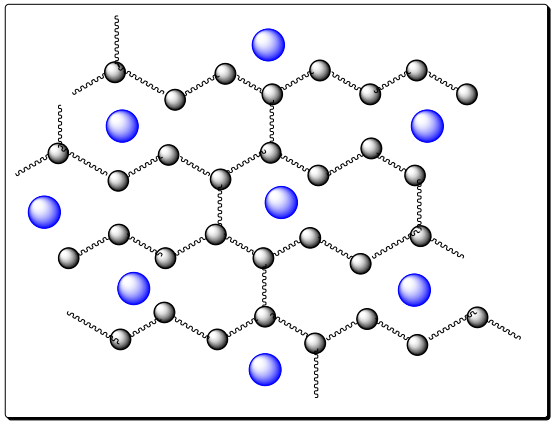
Microporous surface

Porous carbon block with closed surfaces

1. How to increase the surface area .
2. How to regulate the porosity.

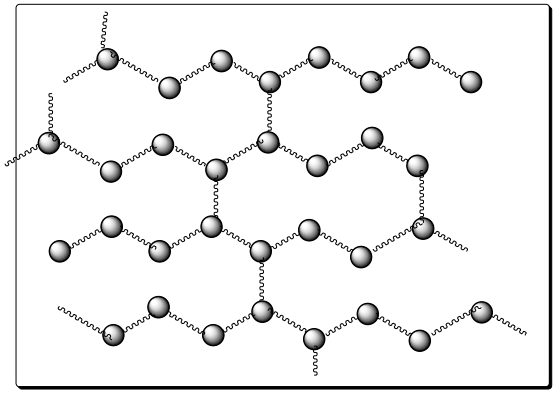
→ Three Approaches

(1) Polymer gel method



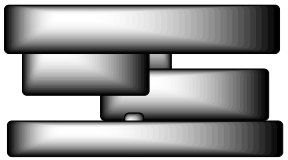
Swelled polymer gel

→

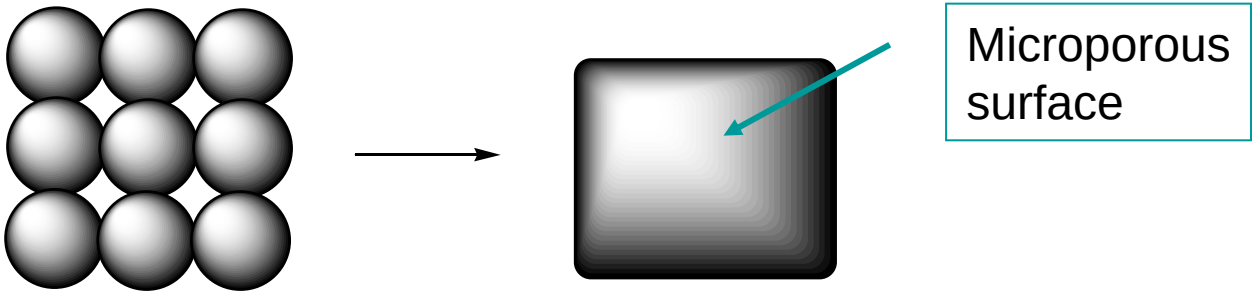


Dried polymer gel (low density)

→

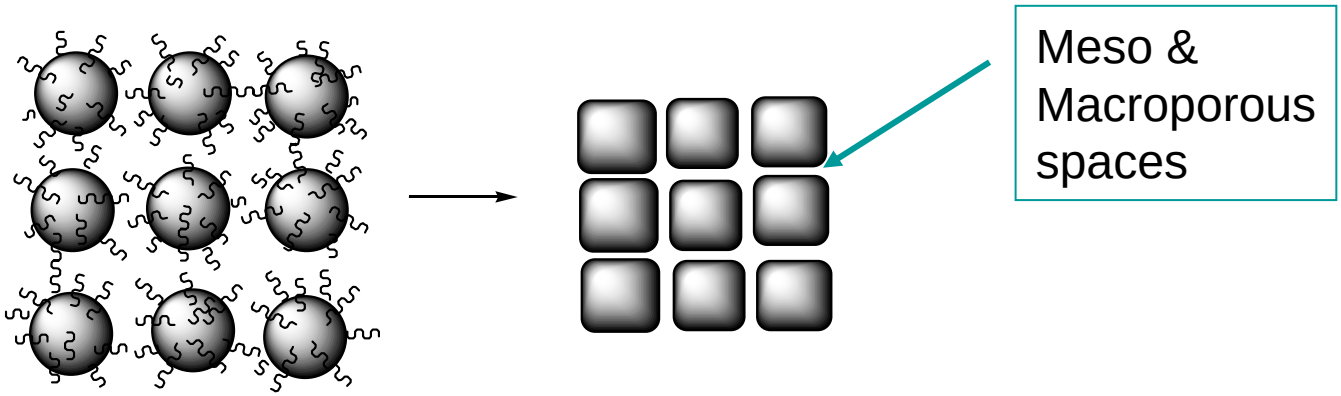


Carbonized polymer gel consisting of Thin carbon blocks



Conventional case: polymer particles are carbonized together to form large carbon blocks consisting of nano-scale basic structural units with cross linking reactions

(2) Micellar method



Polymer particles are isolated each other by micelle formation.
The carbonized blocks must be smaller than the conventional cases.

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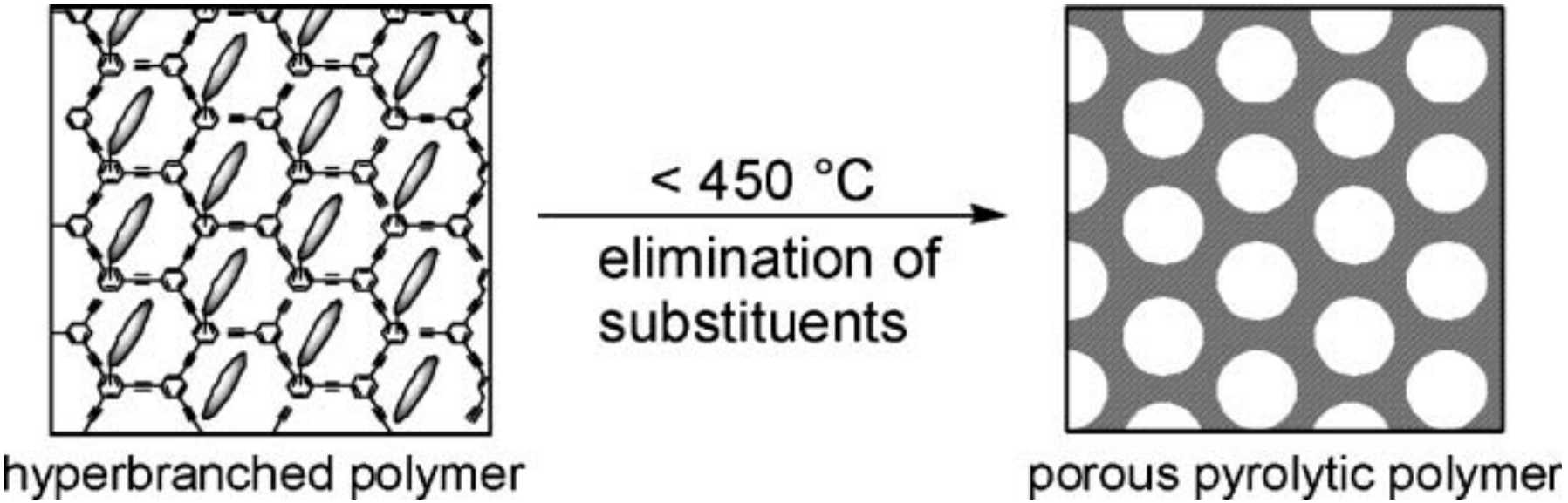
(3) Selective elimination of leaving group from hyper-branched polymer



(rigid frame works)

>900℃

Porous carbon
(microporous)

N. Kobayashi, M. Kijima, J. Mater.Chem., 17 (2007) 4289.

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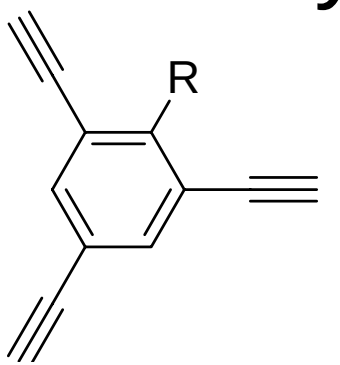
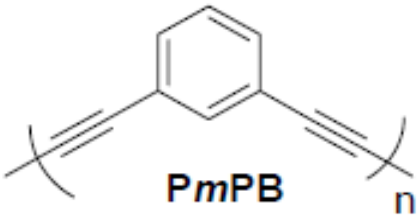
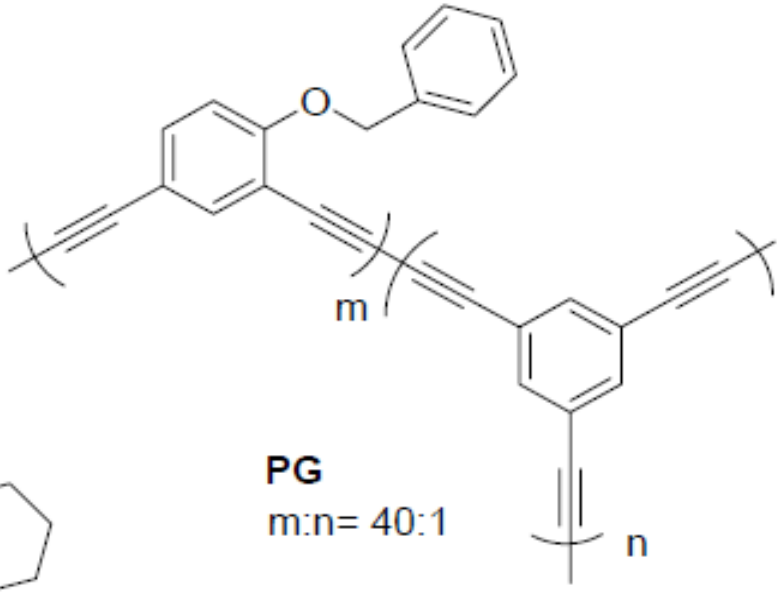
Synthesis of starting polymers

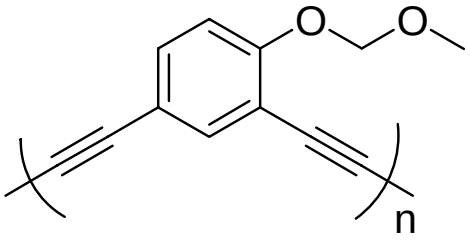


O_2 / Cu-TMEDA cat.

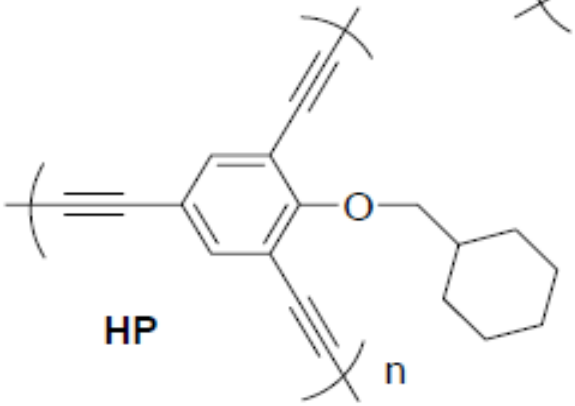
Hay method







Soluble **P*m*PB**



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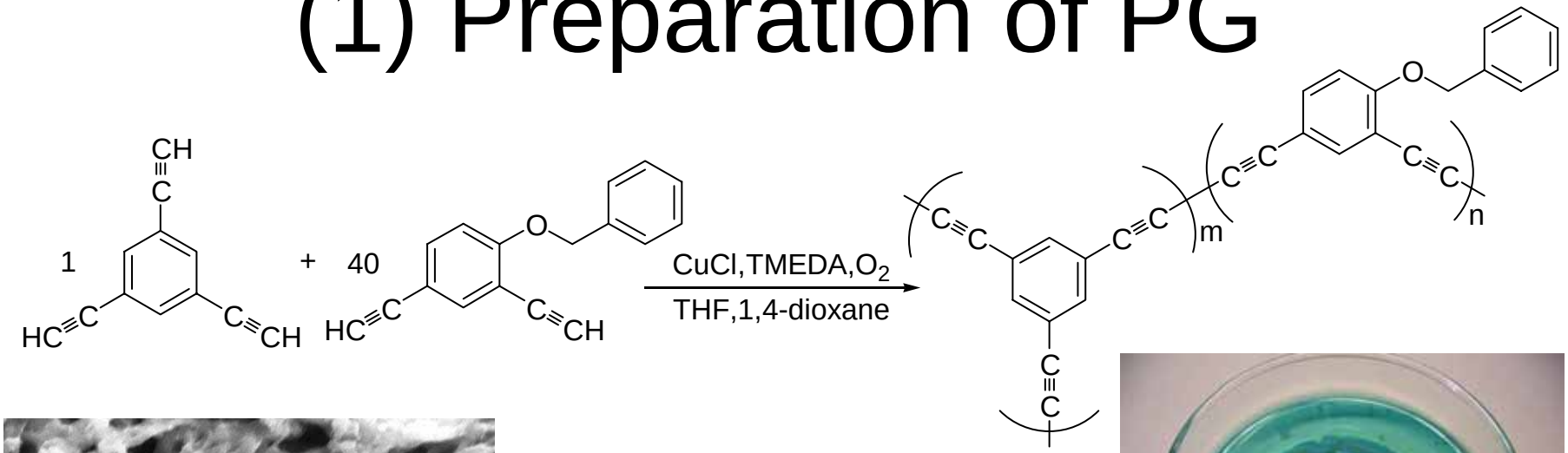
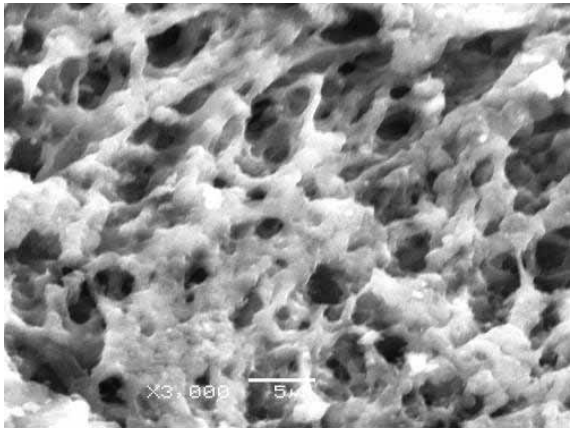
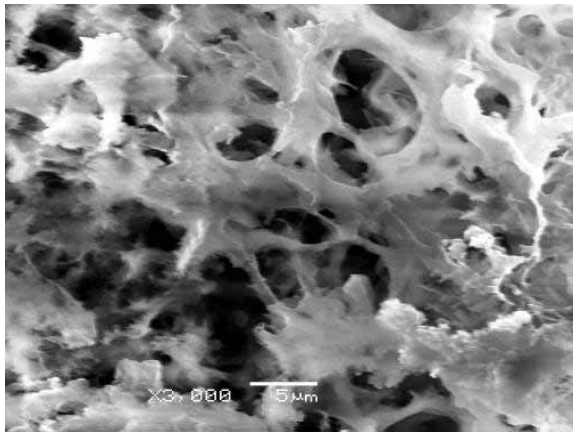
(1) Preparation of PG





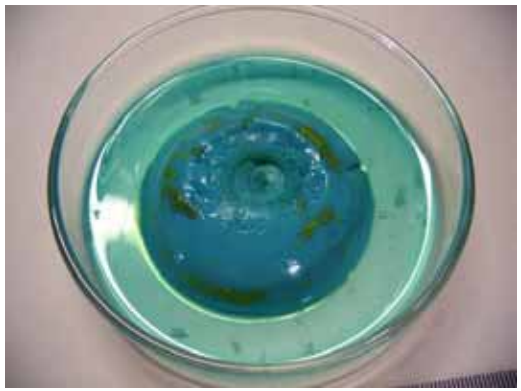
C-PG

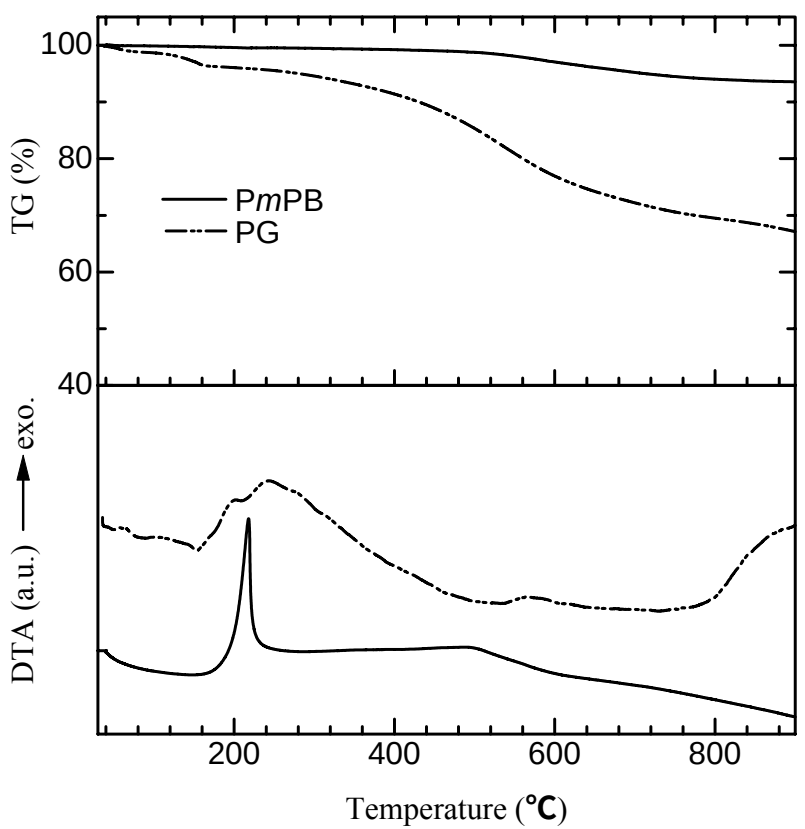
carbonization

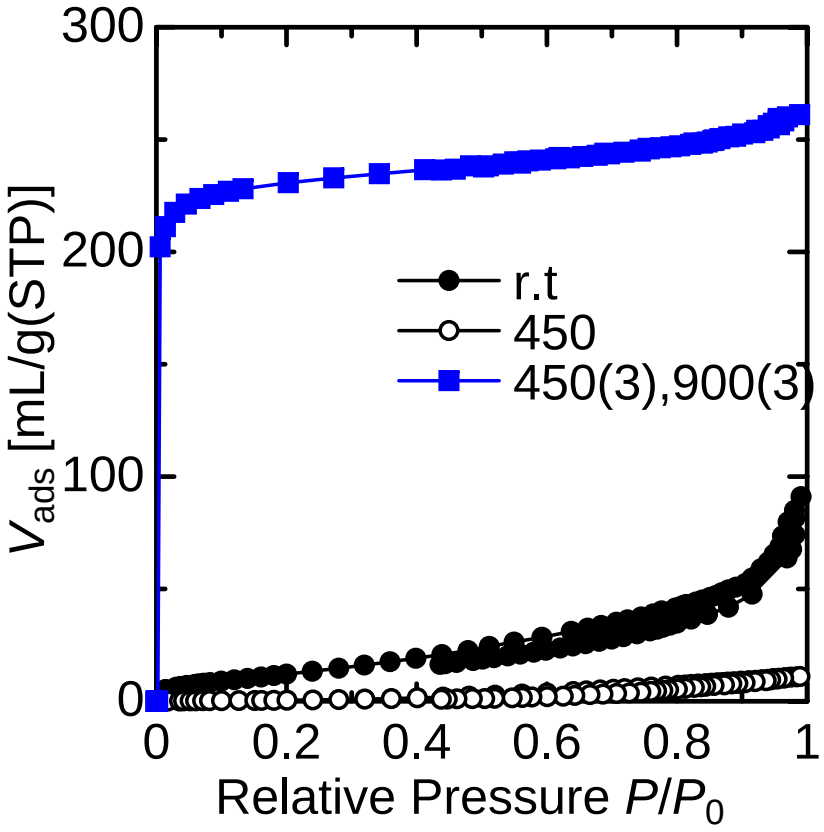


PG (net-like structure)

Freeze dry

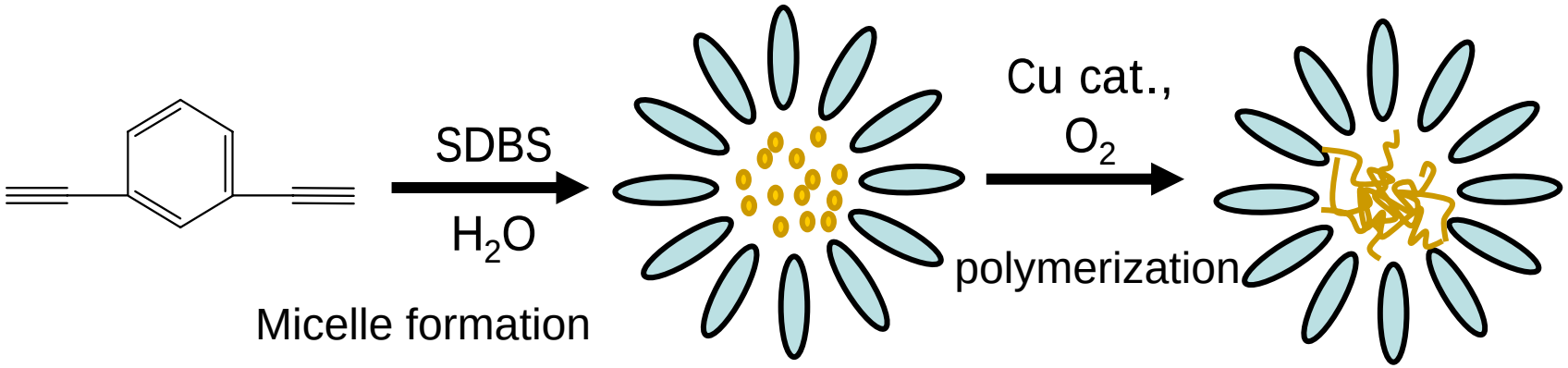


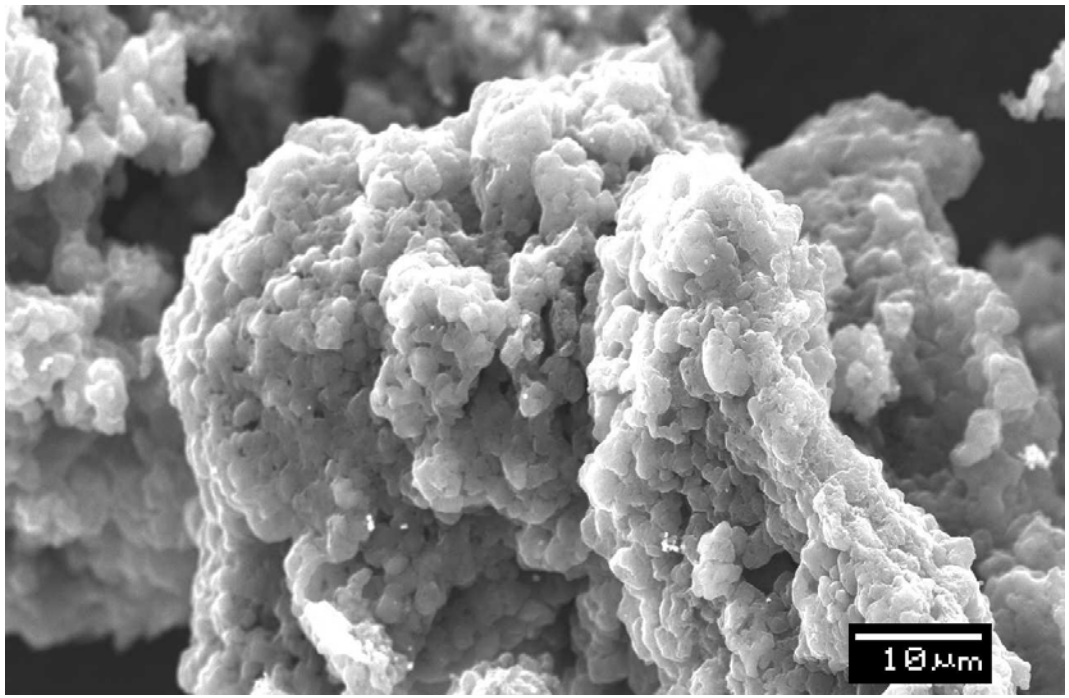




polymer	Conditions	Y (%)	S_{BET} (m^2/g)	$S\alpha_s$ (m^2/g)	V_{micro} (ml/g)	*w* (nm)	V_{meso} (ml/g)	V_{total} (ml/g)
P*m*PB	-	92	470	540	0.2	0.79	0.03	0.28
PG	450(0)	90	2	0	0	—	0.01	0.02
	450(3),900(3)	61	**764**	**1072**	**0.34**	**0.66**	0.04	0.41

(2)-1. Preparation of PM1 and C-PM1





C-PM1

Freeze-dry

carbonization

PM1

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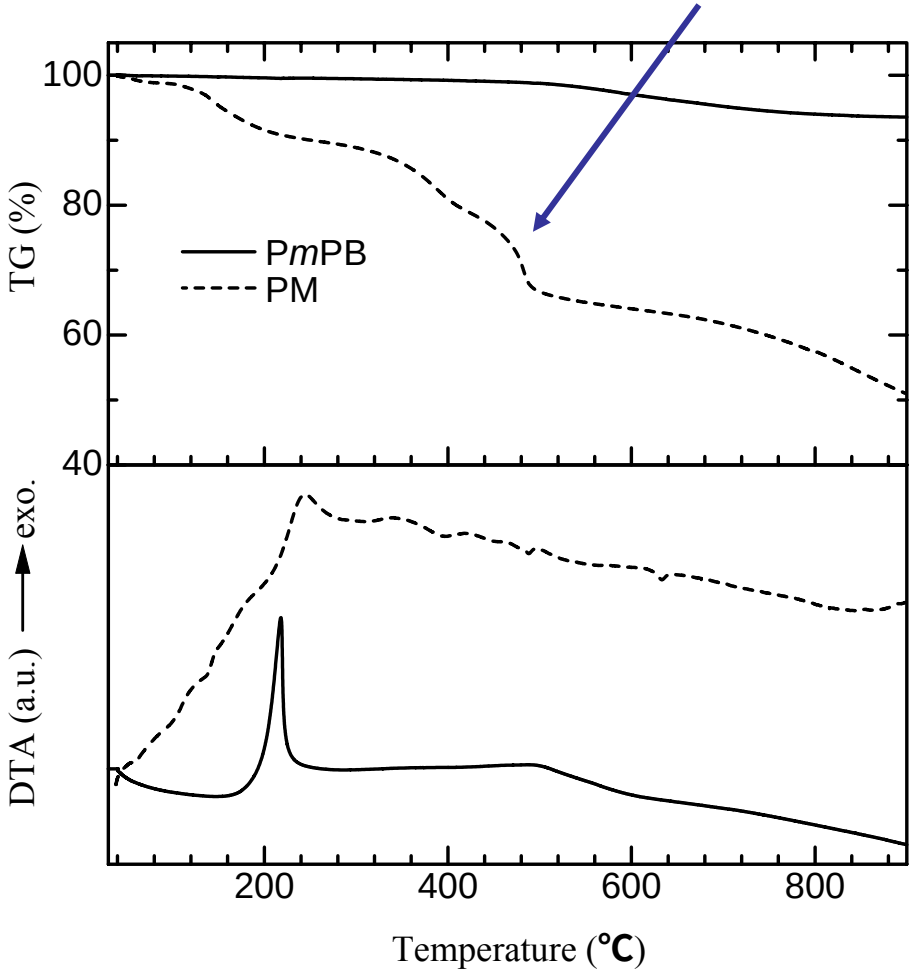
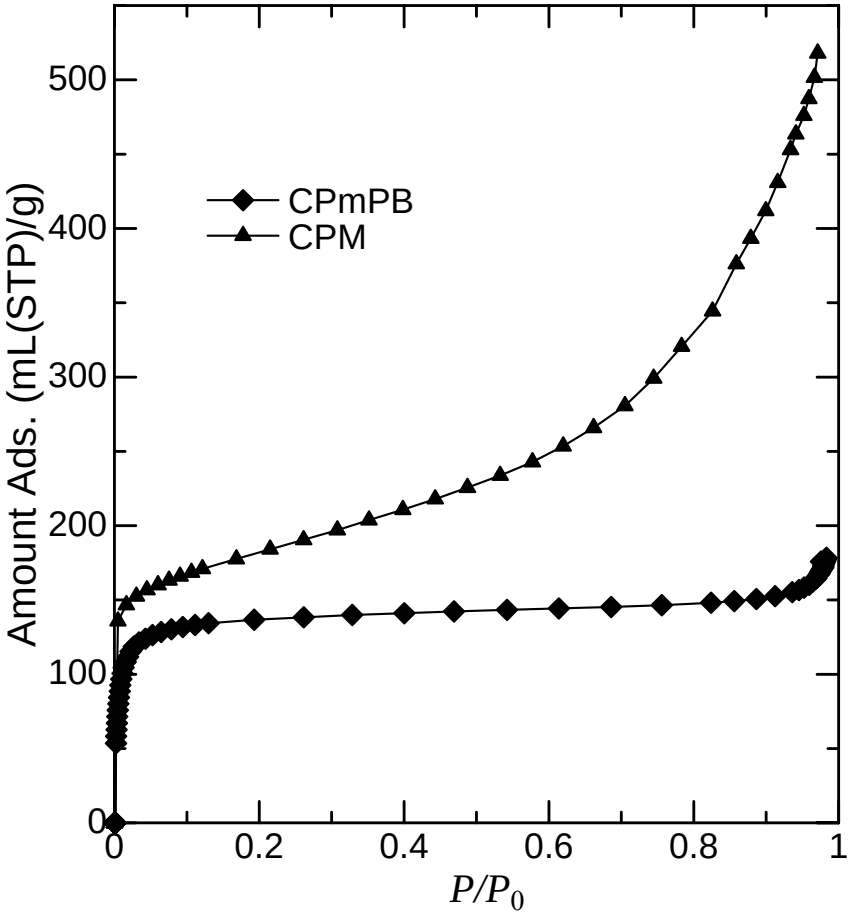
TG/DTA of **PM1** and N_2 adsorption isotherm of **C-PM1**

Degradation and elimination of SDBS





Surface analysis results of **C-PM1**

	water (mL)	BET	α_s			DH		
		S_{total} (m2/g)	S_{total} (m2/g)	V_{micro} (ml/g)	w_{micro} (nm)	V_{meso} (ml/g)	V_{total} (ml/g)	V_{meso}/V_{total} (%)
C-P*m*PB	-	**470**	**540**	**0.2**	**0.79**	**0.03**	**0.28**	**3.8**
C-PM1-6	3	569	693	0.18	0.69	0.21	0.50	42.6
C-PM1-7	20	560	721	0.21	0.68	0.17	0.43	39.3
C-PM1-8	**50**	**638**	**727**	**0.14**	**0.71**	**0.45**	**0.81**	**56.4**
C-PM1-9	100	674	859	0.20	0.64	0.25	0.59	42.1
C-PM1-10*	50	538	630	0.16	0.72	0.28	0.60	46.9

Diethynylbenzene (0.2 mL, 1.6 mmol), CuCl-TMEDA (0.34 mmol), SDBS (35 mg, 0.1mmol)

*: without freeze-drying process

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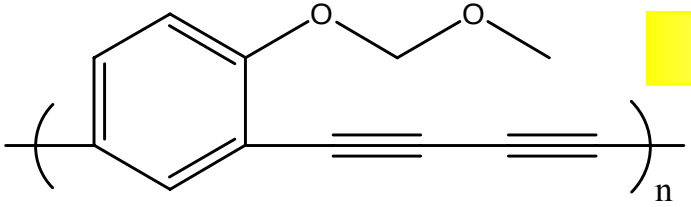
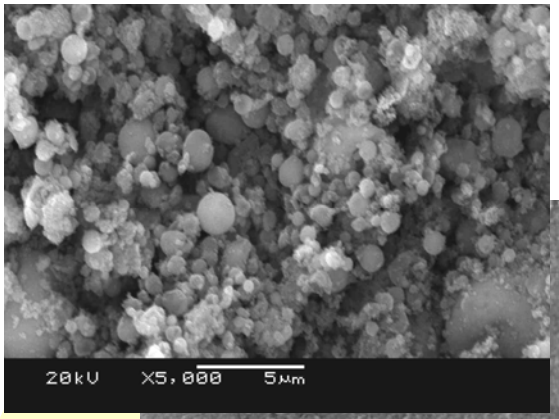
(2)-2. Preparation of PM2 and C-PM2



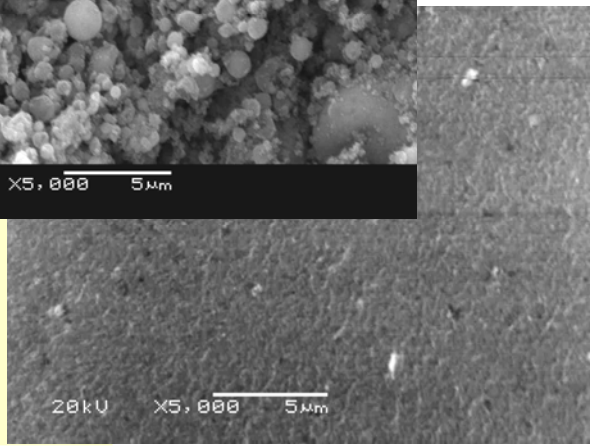
Soluble ***Pm*PB**

Micelle formation

Polymer 50 mg、SDBS 300 mg、
$CHCl_3$ 1 ml、H_2O 6 ml、40 ℃



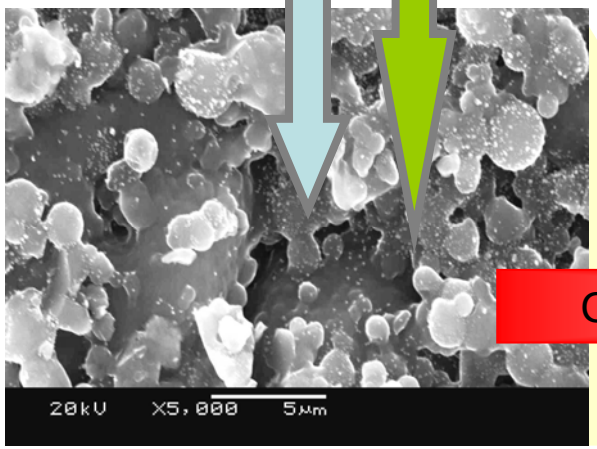
Dispersed image



Packed image

Fused & non-porous C

Precipitation from MeOH **PM2**

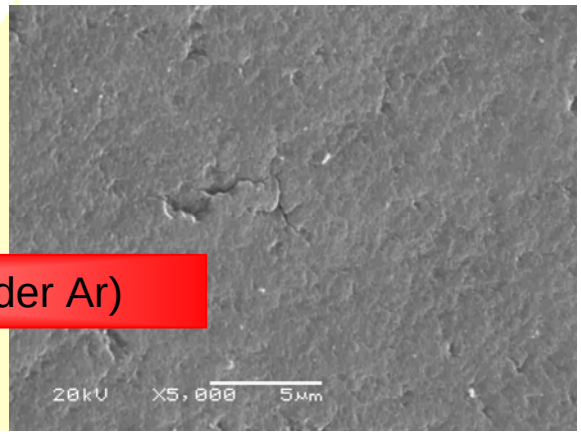


H_2SO_4 tretment

C-P1

C-PM2

Micro&mesoporous C



Carbonization (r.t.→900℃ [10℃/min] under Ar)

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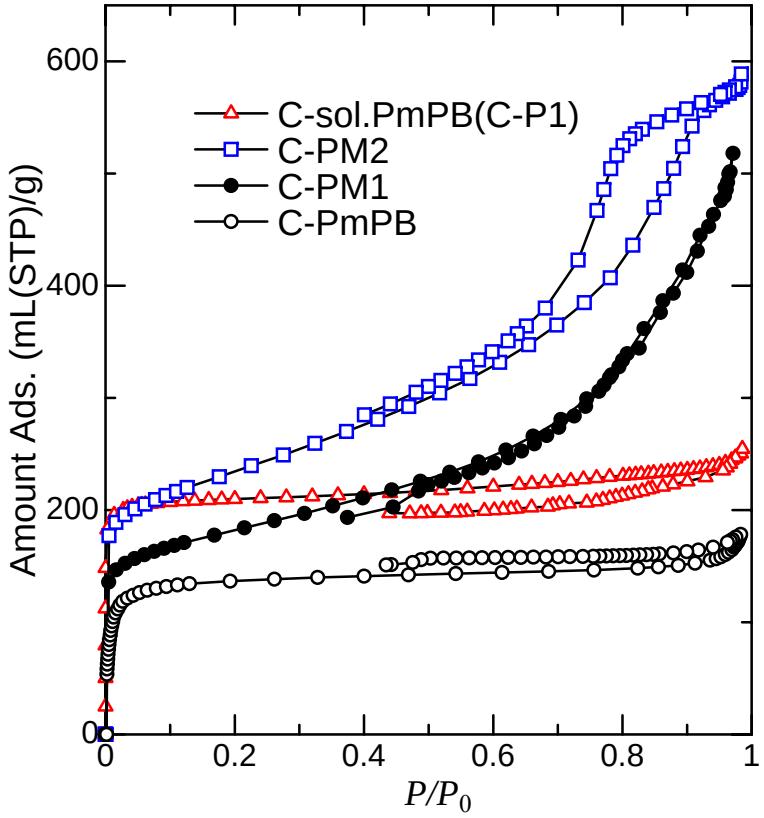
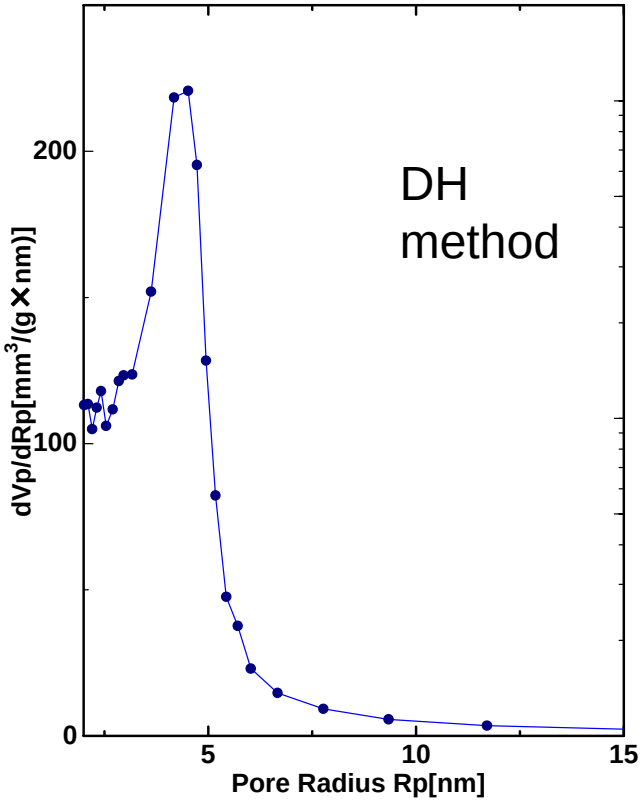
N_2-Adsorption isotherms and pore distribution of **C-PM2**





Sample	C-yield (%)	S_{BET} (m^2/g)	$S_{\alpha s}$ (m^2/g)	w_{micro} (ml/g)	V_{micro} (ml/g)	V_{meso} (ml/g)	V_{total} (ml/g)
C-P1	51.3	714	1028	0.62	0.3	0.06	0.4
C-PM2	**51**	**818**	990	0.59	0.15	**0.45**	**0.92**

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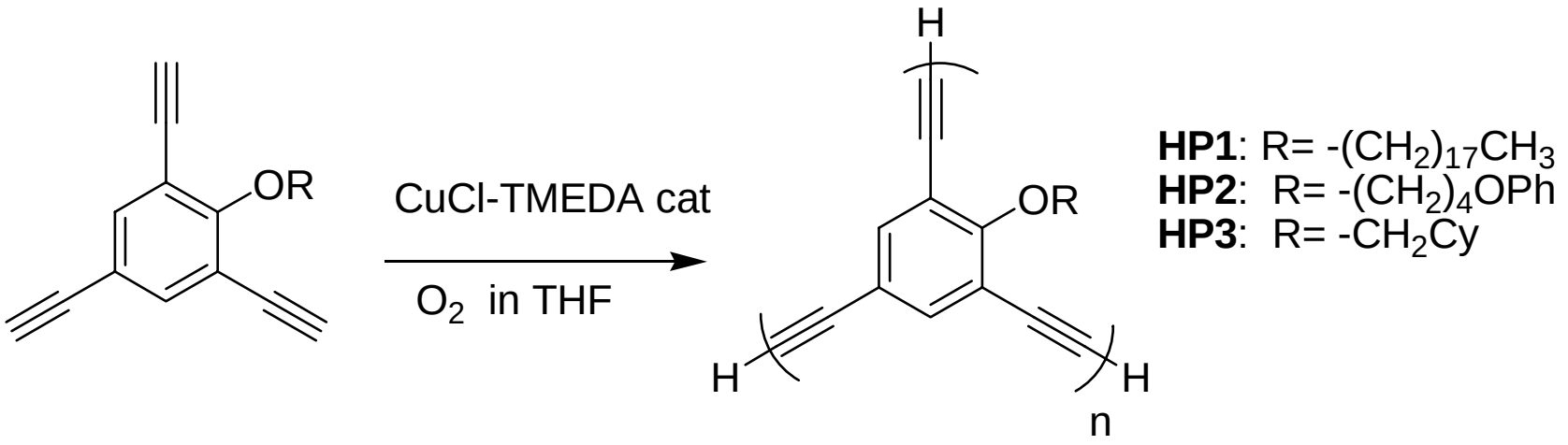
(3) Synthesis of HP



HP1: R= -$(CH_2)_{17}CH_3$
HP2: R= -$(CH_2)_4OPh$
HP3: R= -CH_2Cy

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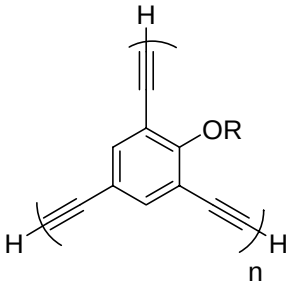
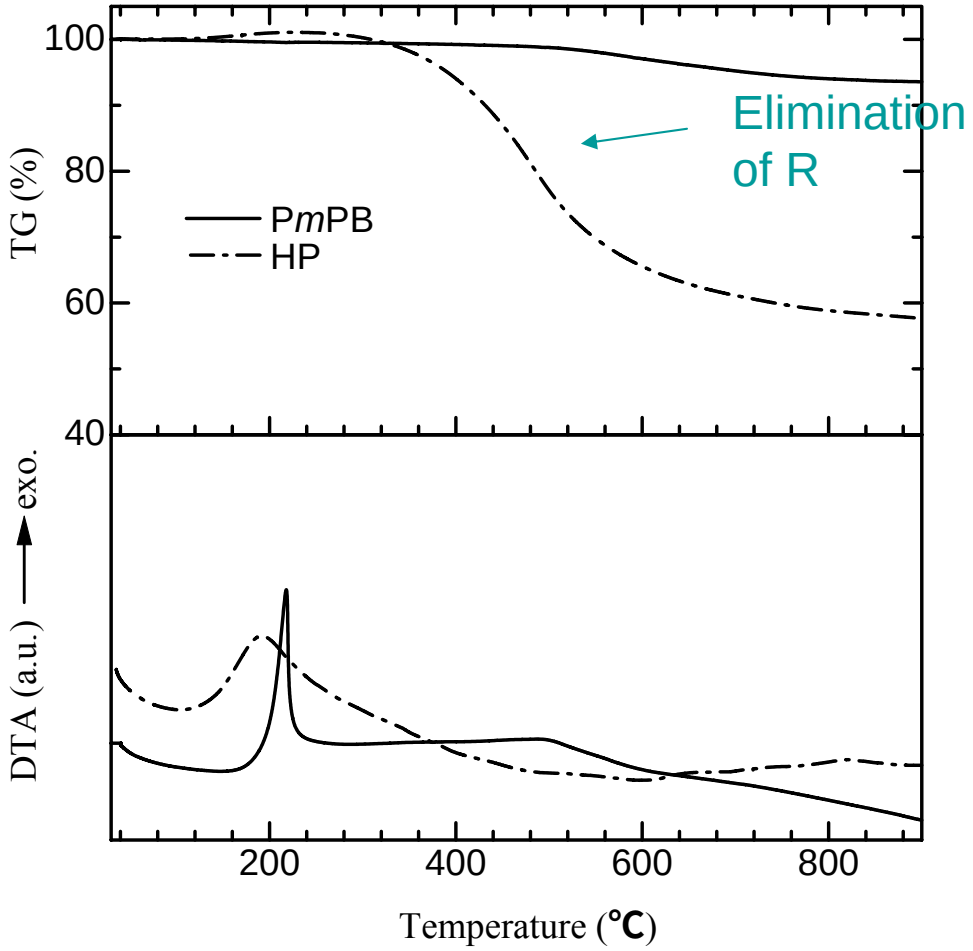
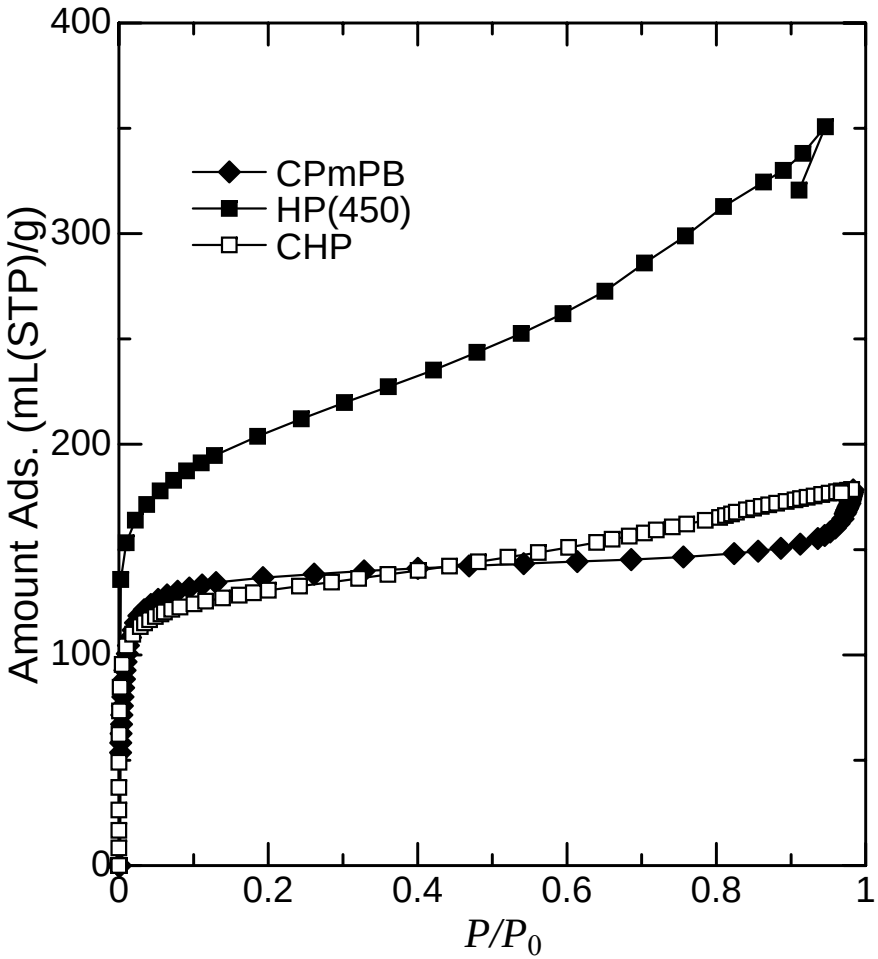
HP3(cyclohexylmethyl)





TG/DTA



N_2-adsorption isotherm

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Surface analysis data of HP and CHP

Material	Y (%)	α_s			DH		
		S_{total} (m2/g)	V_{micro} (ml/g)	W_{micro} (nm)	V_{meso} (ml/g)	V_{total} (ml/g)	V_{meso}/V_{total} (%)
CP*m*PB	**92**	**540**	**0.2**	**0.79**	**0.01**	**0.28**	**3.8**
HP1(450)	43	260	0.10	0.99	0.01	0.18	3.1
CHP1	39	2	-	-	-	0.05	-
HP2(450)	69	**940**	0.26	0.67	**0.16**	0.51	32
CHP2	59	820	0.23	0.63	0.09	0.40	22
HP3(450)	69	**820**	0.21	0.75	**0.14**	0.55	26
CHP3	67	560	0.16	0.70	0.05	0.28	17

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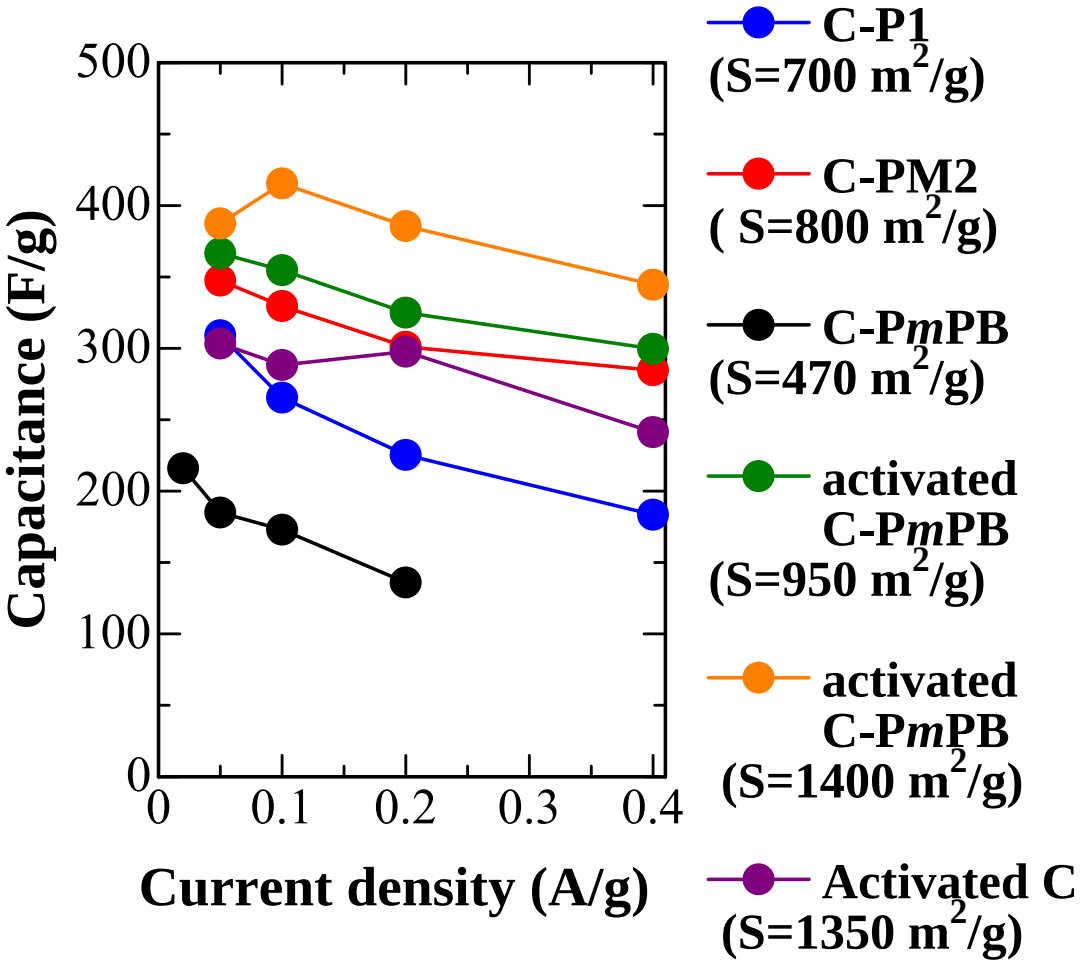
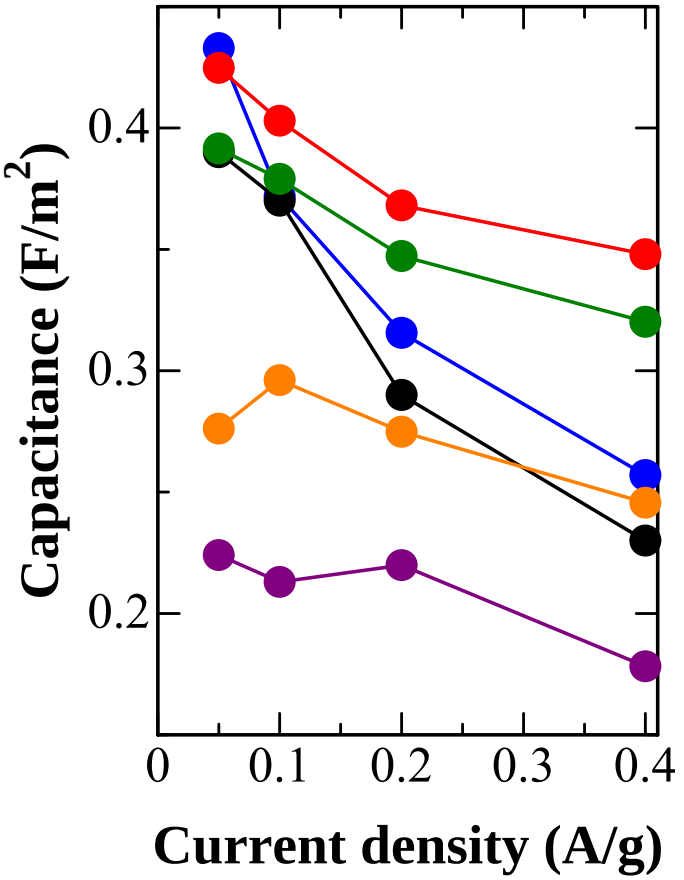
Electrical Double Layer Capacitances of **C-P*m*PBs** (three-electrode system in 1M H_2SO_4)





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(1) Pyrolytic conversion of structured poly(*m*-phenylenebutadiynylene)s **P*m*PBs** to porous C

(2) Pyrolytic conversion of structured Lignin-Cellulose composites to porous C

(3) Pyrolytic conversion of MOFs and COFs to porous C

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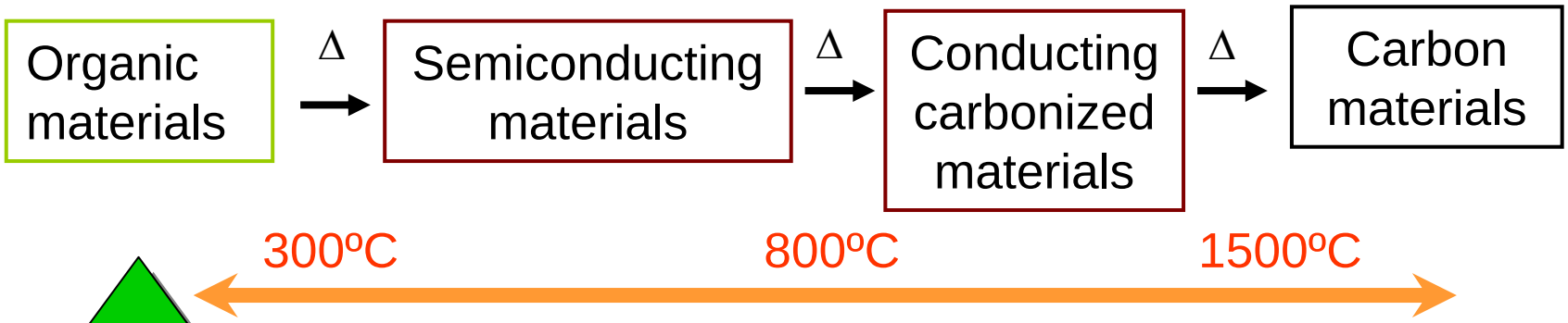
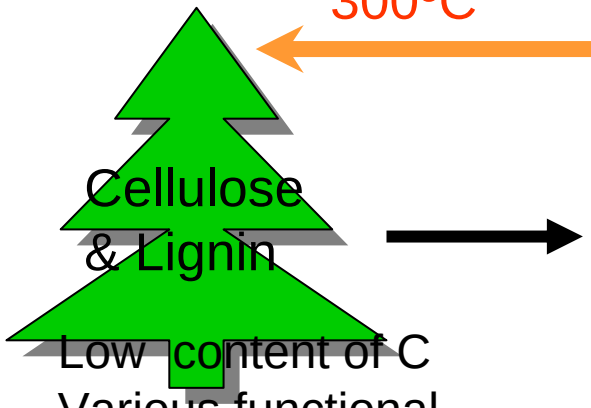
Purpose of our research

Synthesis of functional carbon-rich materials from wooden biomass without production of CO_2





Low content of C
Various functional groups in the material

Possible to restructurize

Structured C-rich Materials
High-C content: uniform & homogeneous composition

Application: thermoelectric-conversion, Photovoltaic & sollar cells, electrodes for batteries, fuel cell, EDLC, Stable porous Energy-source (H_2 etc) storage material etc.

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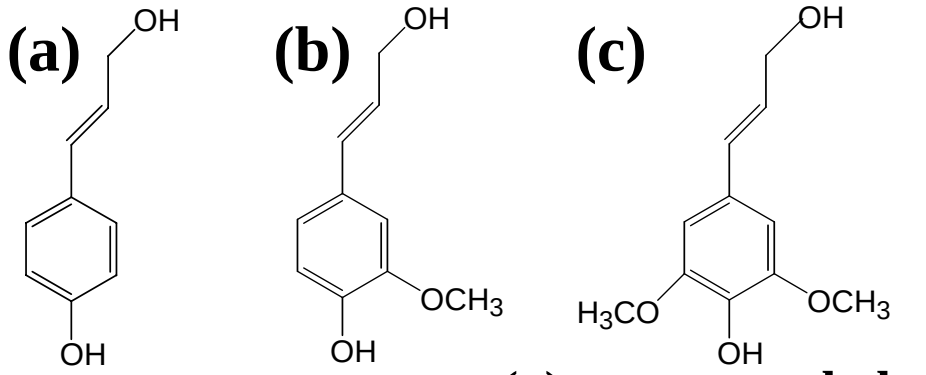
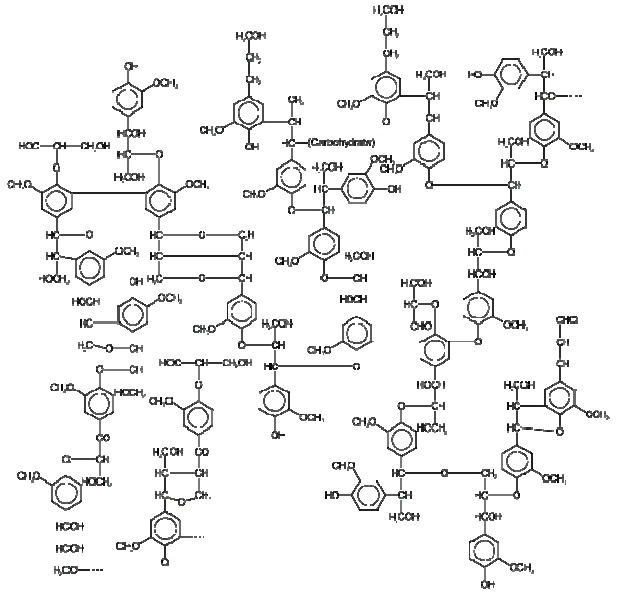
Lignin

<aromatic structural unit>



(a) *p*-coumaryl alcohol
(b) coniferyl alcohol
(c) sinapyl alcohol

<a possible structure>



Advantage of lignin to convert into carbon materials:
Lignin has the phenolic components: high C fixation ability on anaerobic pyrolysis

There has been reported several results on carbonization of lignin and preparation of activated carbon

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Alkaline Lignin

Black powder,
Water soluble

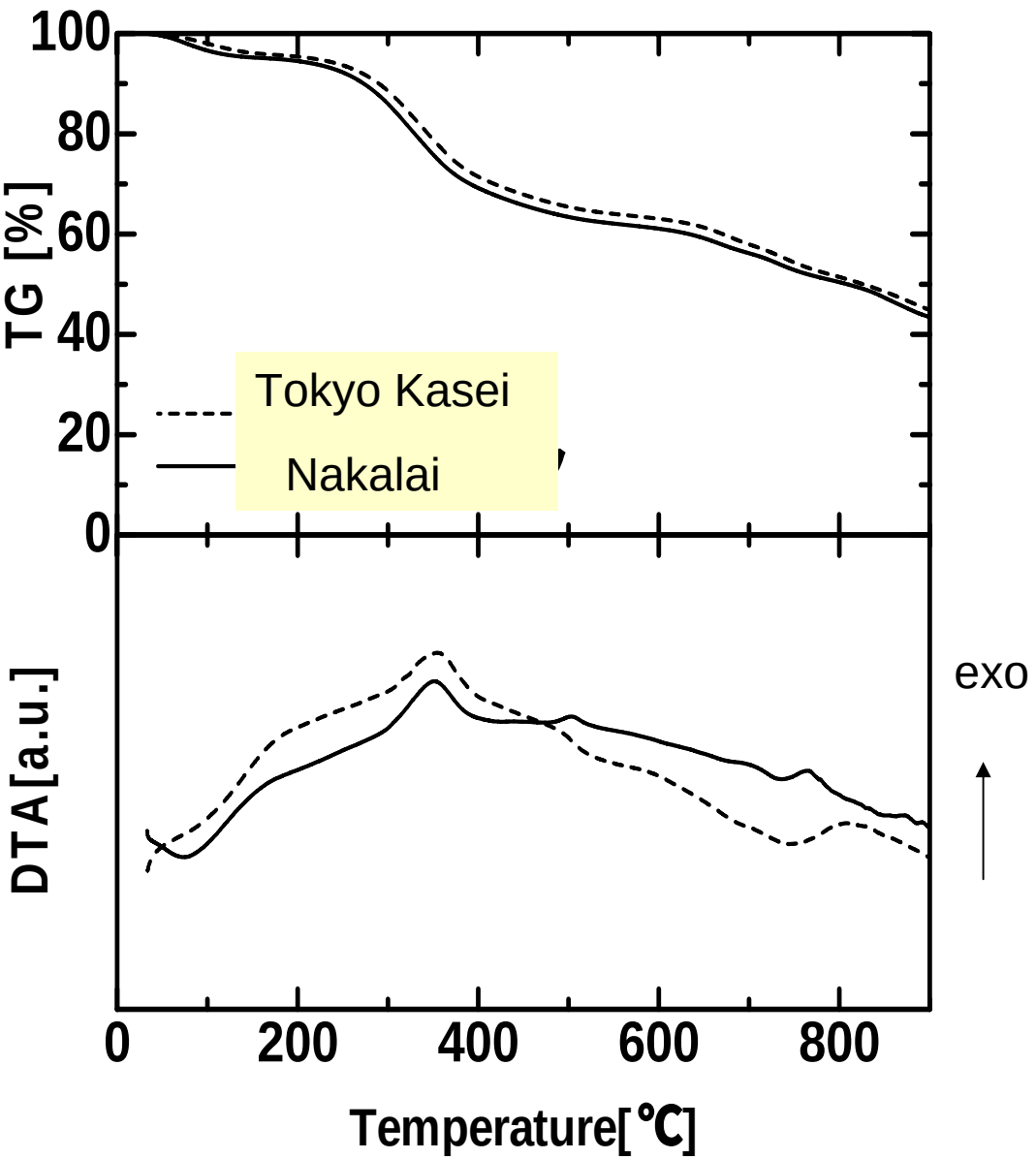
Elemental analysis

C: 51.72 %, H: 5.12 %, N: 0.13 % (Nacalai),

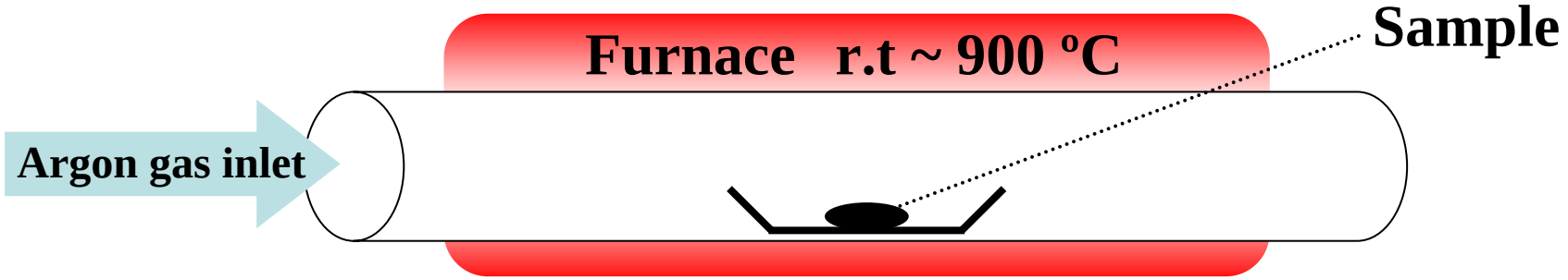
C: 51.83 %, H: 4.78 %, N: 0.11 % (Tokyo Kasei)

Reagent grade (available)

M 350 g/mol
(cryoscopic method)



① Carbonization of alkaline lignin



Carbonization conditions

(annealing time)

CL1:	r.t ~ 900 °C	10 °C/min			
CL2:	r.t ~ 900 °C	4 °C/min			
CL3:	r.t ~ 900 °C	2 °C/min			
CL4:	r.t ~ 900 °C	1 °C/min			
CL5:	r.t ~ 300 °C	10 °C/min	300 °C (1)	300 °C ~ 900 °C	10 °C/min
CL6:	r.t ~ 350 °C	10 °C/min	350 °C (1)	350 °C ~ 900 °C	10 °C/min
CL7:	r.t ~ 350 °C	10 °C/min	350 °C (2)	350 °C ~ 900 °C	10 °C/min
CL8:	r.t ~ 350 °C	10 °C/min	350 °C (3)	350 °C ~ 900 °C	10 °C/min

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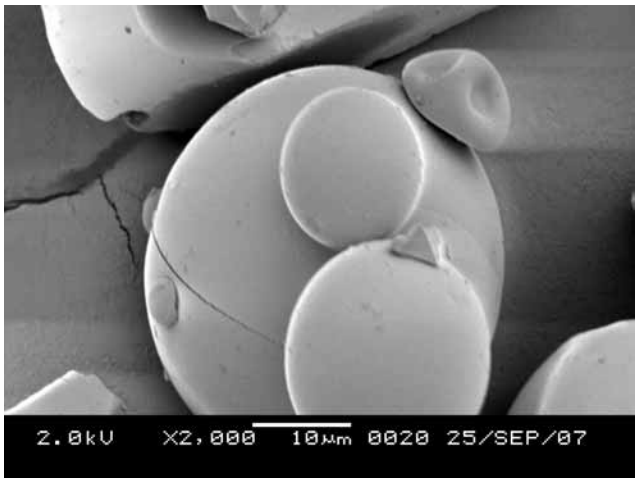
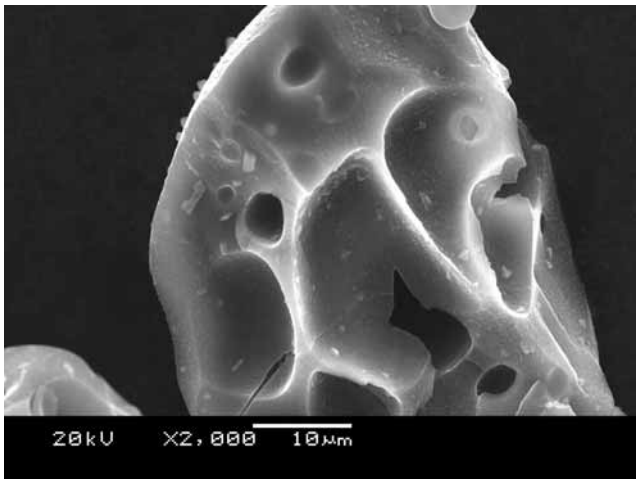
SEM



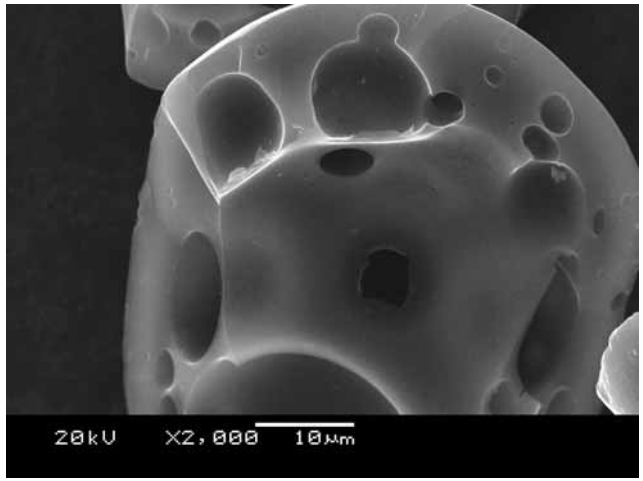
10 μm

Alkaline lignin



10 μm

CL4



10 μm

CLW

CL4：deposition on the surface was a Na salt confirmed by XPS

CLW：After washing **CL4** with water, the deposition was cleaned off

Carbonization results and N_2 adsorption data

sample	Yield (%)	S_{BET} (m^2/g)	α_s			V_{total} (ml/g)	DH	
			S_{total} (m^2/g)	V_{micro} (ml/g)	W_{micro} (nm)		V_{meso} (ml/g)	V_{meso}/V_{total} (%)
CL4	**46**	**664**	**655**	**0.09**	**0.90**	**0.55**	**0.15**	**28**
CLW	**—**	**899**	**1031**	**0.17**	**0.65**	**0.69**	**0.19**	**27**

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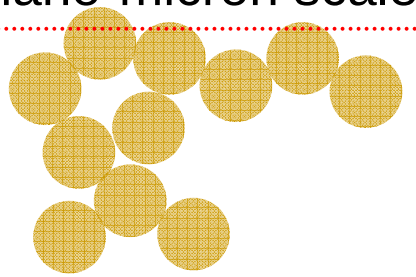
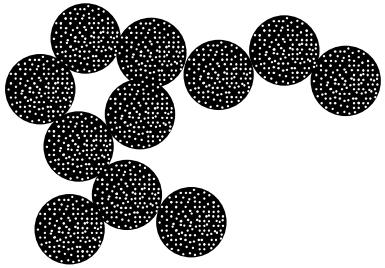
Control of structure and morphology of carbonized materials

Particles in nano-micron scale



carbonization

Microporous C-particles

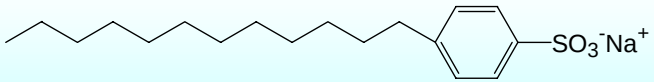


Aims: 1) Increase of effective surface area. (external)

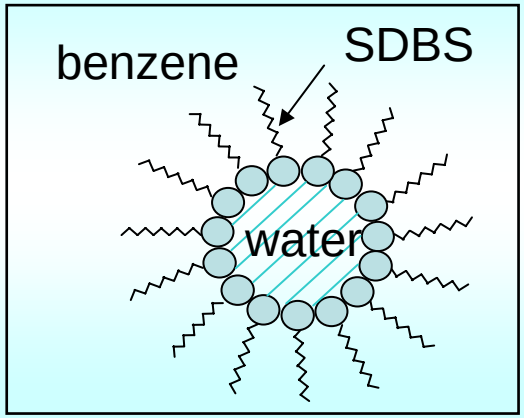
2) Generation of new pore space between the particles

Typical conditions

	Water (ml)	SDBS (mg)	Benzene (ml)
ML3	5	50	45



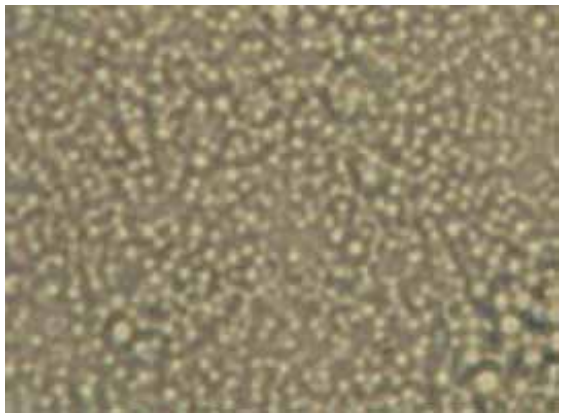
Sodium Dodecylbenzenesulfonate(SDBS)



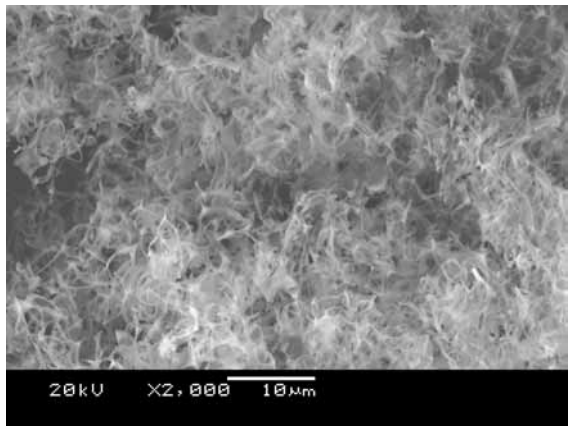
Reverse micelle

② Preparation of micellar lignins and the carbonization

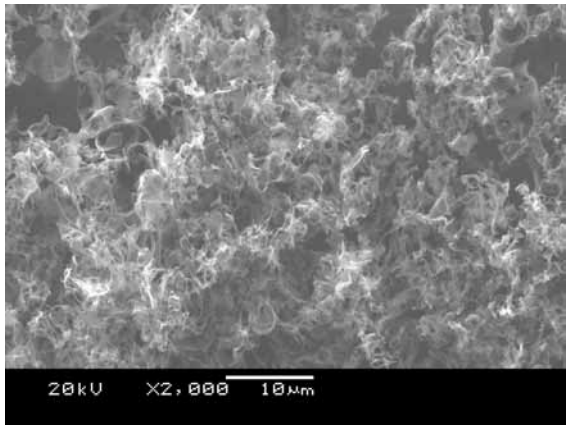
Preparation of micellar lignins (ML) and their carbonization



(in solution)

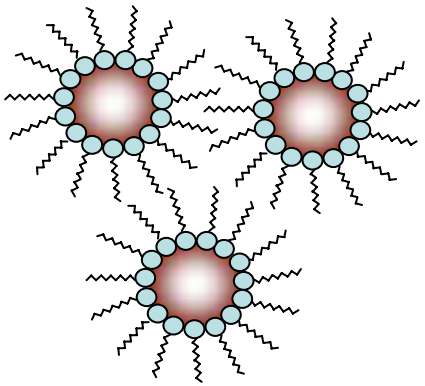


(freeze-dried)

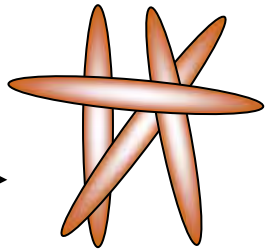


10 μm

ML3



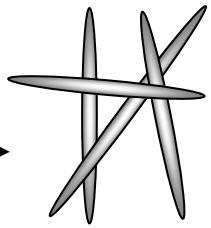
Freeze-dried



Fine-structured ML

CML3

carbonization

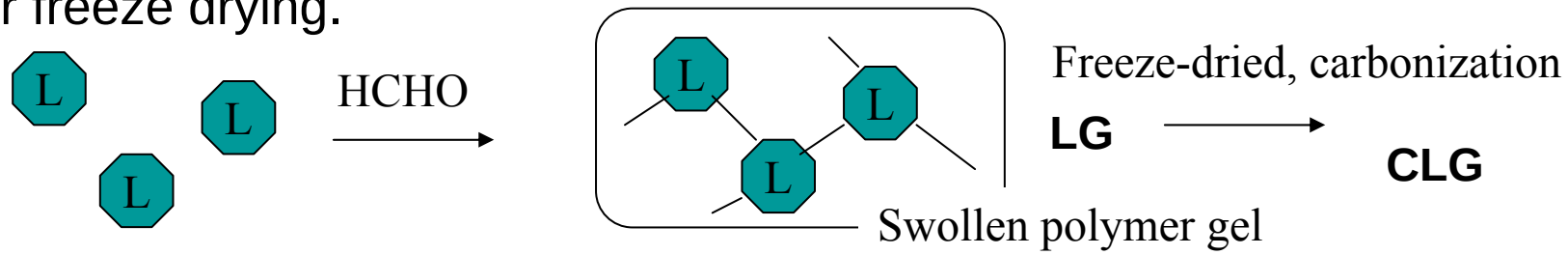


Particle samples could not be obtained in this case.
In order to obtain particle lignins, (3) rigid lignin gels are synthesized

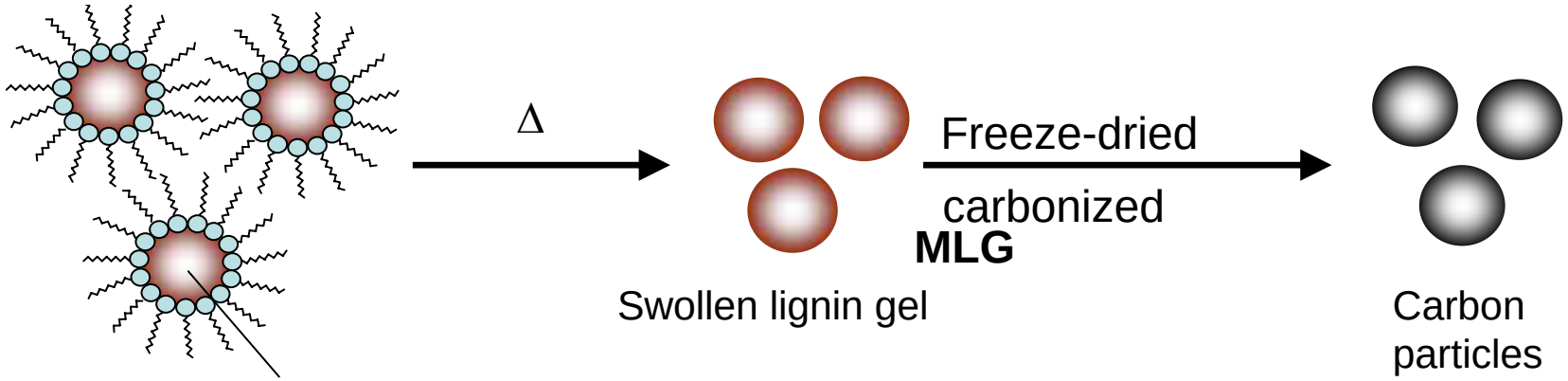
Toward synthesis of carbonized lignin particles

③ Preparation of alkaline lignin gel and the carbonization

Under basic aqueous conditions, alkaline lignin was reacted with formaldehyde to give a swelled polymer gel, which was carbonized after freeze drying.



④ Preparation of lignin-gel particles and their carbonization



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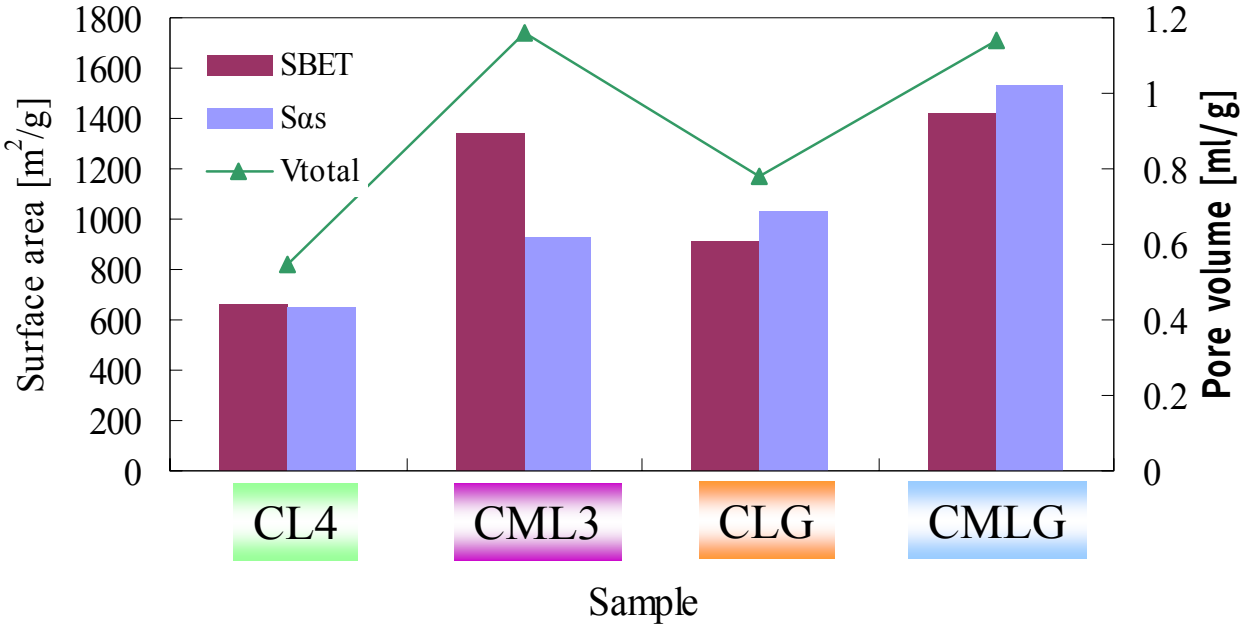
Carbonization and N_2 adsorption results

sample	Yield (%)	S_{BET} (m^2/g)	α_s			V_{total} (ml/g)	DH	
			S_{total} (m^2/g)	V_{micro} (ml/g)	W_{micro} (nm)		V_{meso} (ml/g)	V_{meso}/V_{total} (%)
CL4	45	738	920	0.26	0.70	0.50	0.06	11
CML3	17	1340	928	0.19	1.14	1.16	0.45	39
CLG	42	915	1029	0.17	0.70	0.78	0.23	30
CMLG	29	**1423**	**1528**	0.28	0.78	**1.14**	0.30	26



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(1) Pyrolytic conversion of structured poly(*m*-phenylenebutadiynylene)s **P*m*PBs** to porous C

(2) Pyrolytic conversion of structured Lignin-Cellulose composites to porous C

(3) Pyrolytic conversion of MOFs and COFs to porous C

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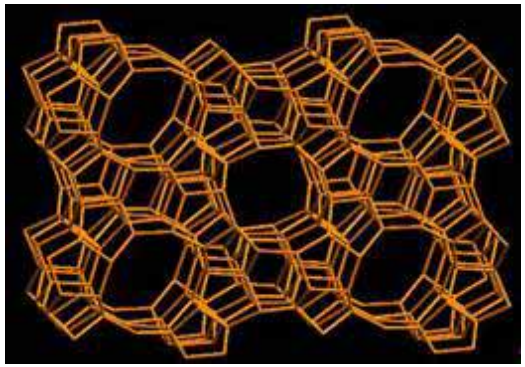
Porous materials

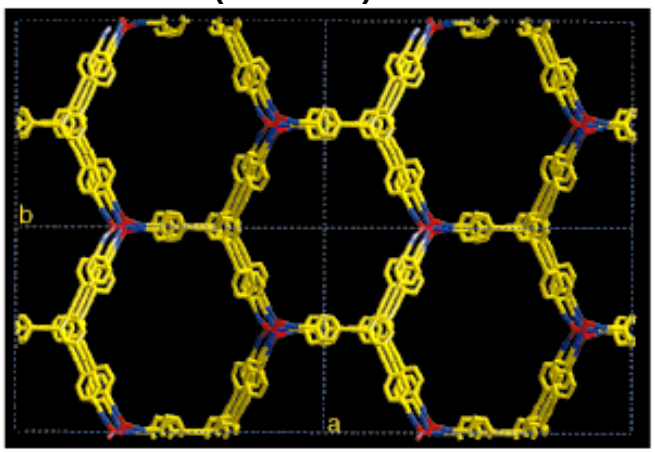
Adsorbent, Catalyst, Catalyst support, Electrode(carbon)

Inorganic materials
Zeolite, porous silica
Corroded metals



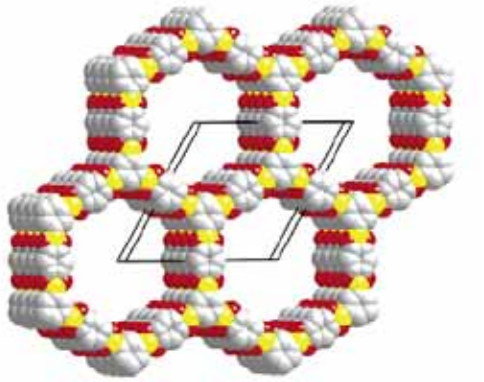
Carbon materials
Activated carbons
Template carbons
Pyrolytic carbons

Coordination polymers
Metal organic frameworks
(MOFs)



MOF-177 (4500 $m^2 g^{-1}$, Langmuir)
MIL-101 (5900 $m^2 g^{-1}$, Langmuir),

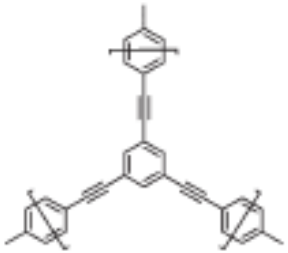
Organic zeolite, COF,
Microporous polymers



COF-103 (4210 $m^2 g^{-1}$, BET)
PAF-1 (5600 $m^2 g^{-1}$,BET)

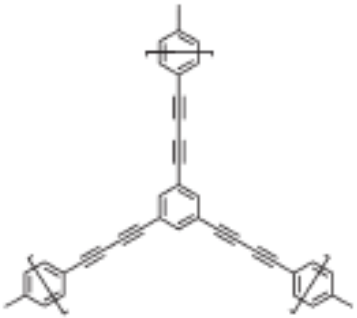
Chemically, physically Stable, electrical conductive

Conjugated microporous polymers



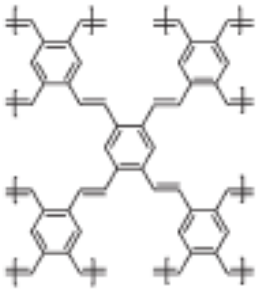
CMP-1

Microporous; SA_{BET} = 834 m^2/g;
MPV = 0.33 cm^3/g; pore size ~ 1 nm[1,2]



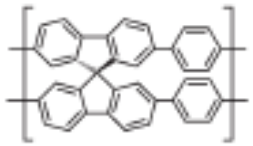
HCMP-1

Micro/mesoporous; SA_{BET} = 842 m^2/g
PV_{tot} = 1.16 cm^3/g; pore size ~ 1-5 nm[4]



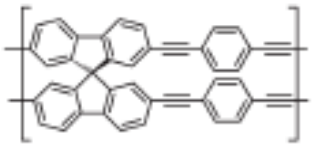
PPV network

Mesoporous; SA_{BET} = 761 m^2/g
PV_{tot} = 1.16 cm^3/g; pore size ~ 5.6 nm[6]



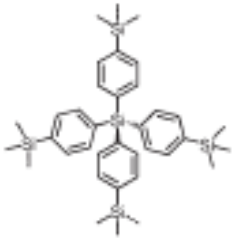
P1

Microporous; SA_{BET} = 450 m^2/g[3]



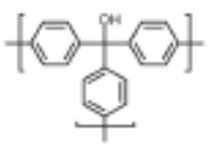
P2

Microporous; SA_{BET} = 510 m^2/g[3]



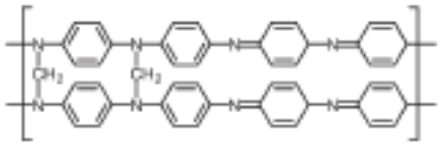
EOF-1

Microporous; SA_{BET} = 780 m^2/g
MPV = 0.32 cm^3/g[5]



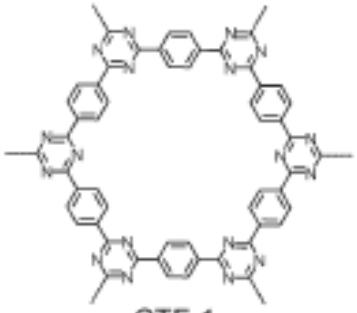
Carbinol HCP

Mesoporous; SA_{BET} up to 1000 m^2/g[30]



Polyaniline HCP

Meso/macroporous; SA_{BET} up to 632 m^2/g
PV_{tot} = 0.94 cm^3/g[7]



CTF-1

Microporous; SA_{BET} = 711 m^2/g
PV_{tot} = 0.40 cm^3/g; pore size ~ 1.2 nm[8]

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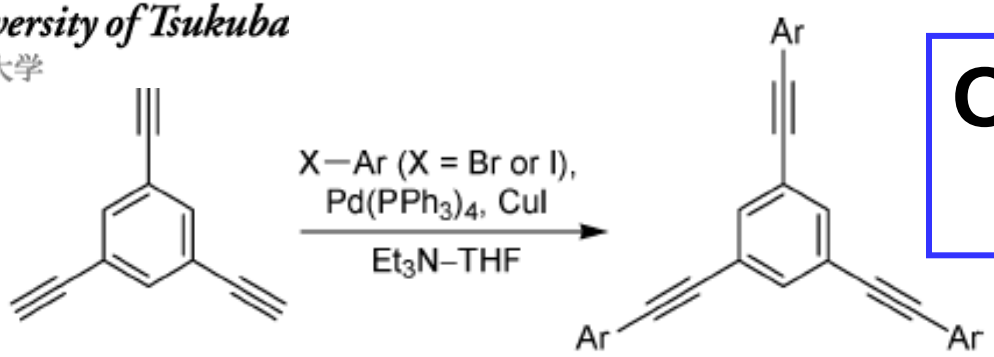
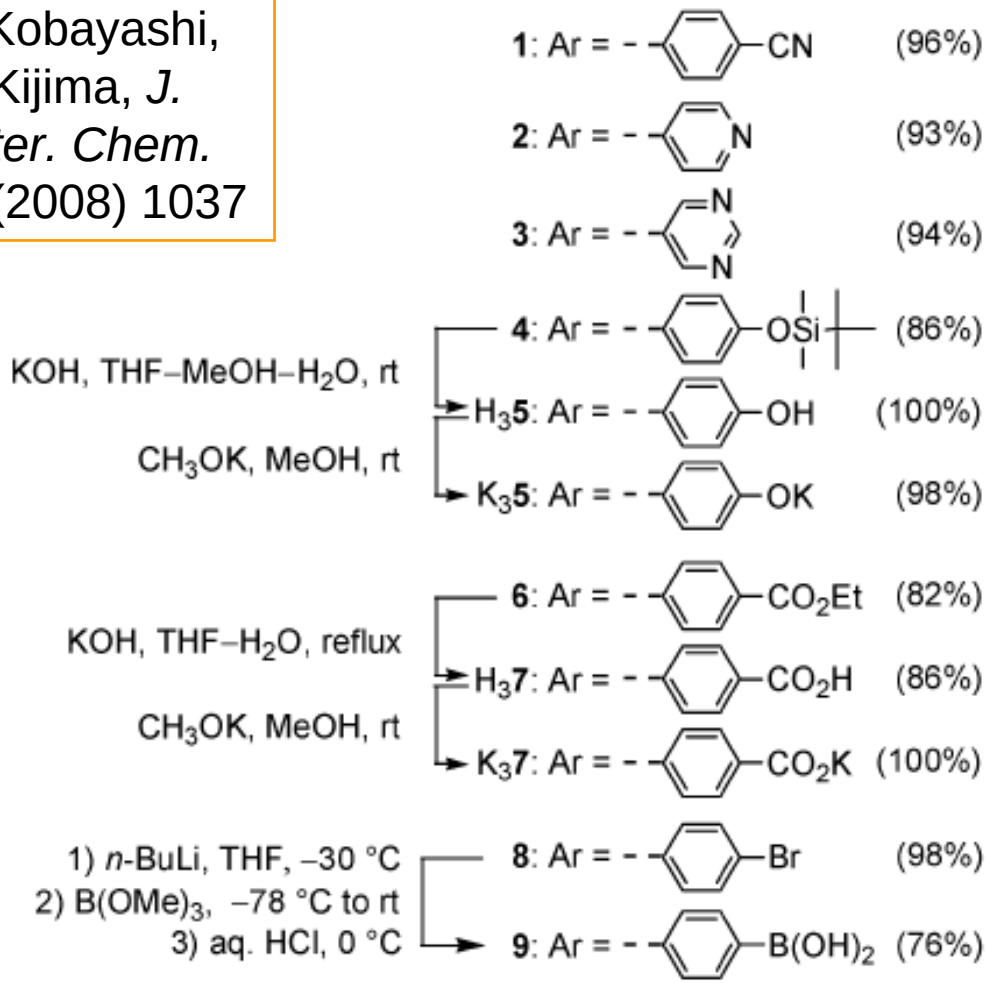
Organic Linkers
TPEB



N. Kobayashi, M. Kijima, *J. Mater. Chem.* **18** (2008) 1037

Good carbonization yields and high S_{BET}



82%	495 m^2/g	
84	113	
70	459	
59	840	
56	1040	
53	67	
53	534	
77	150	

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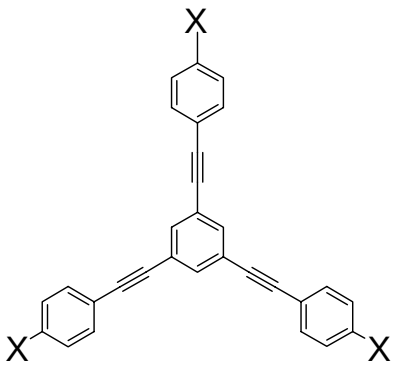
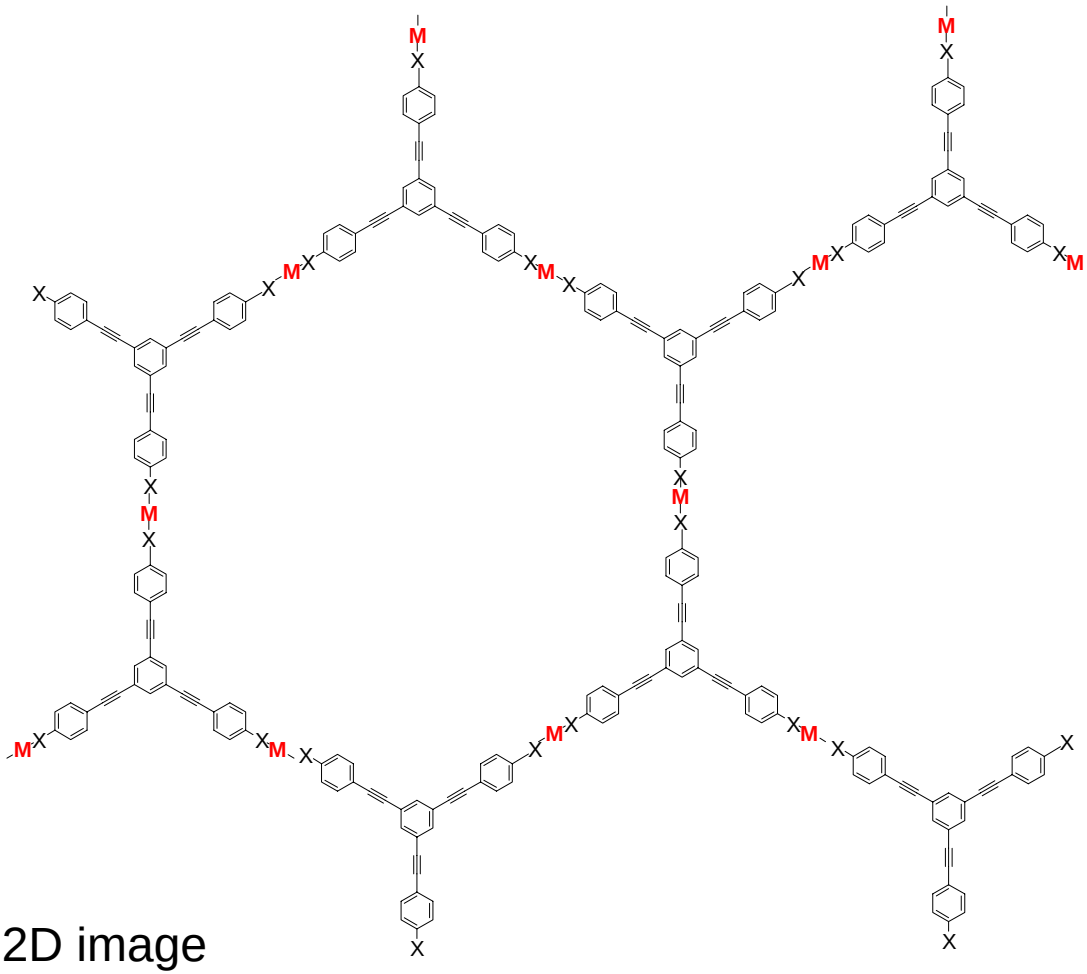
Image of MOF constructing from the organic linker(TPEB) and metal ion



TPEB

+

Metal ion



2D image

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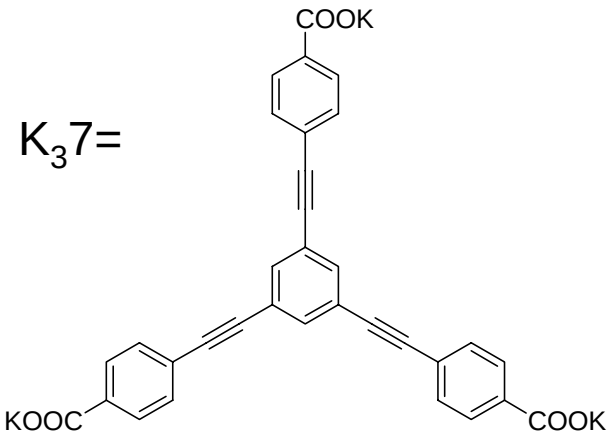
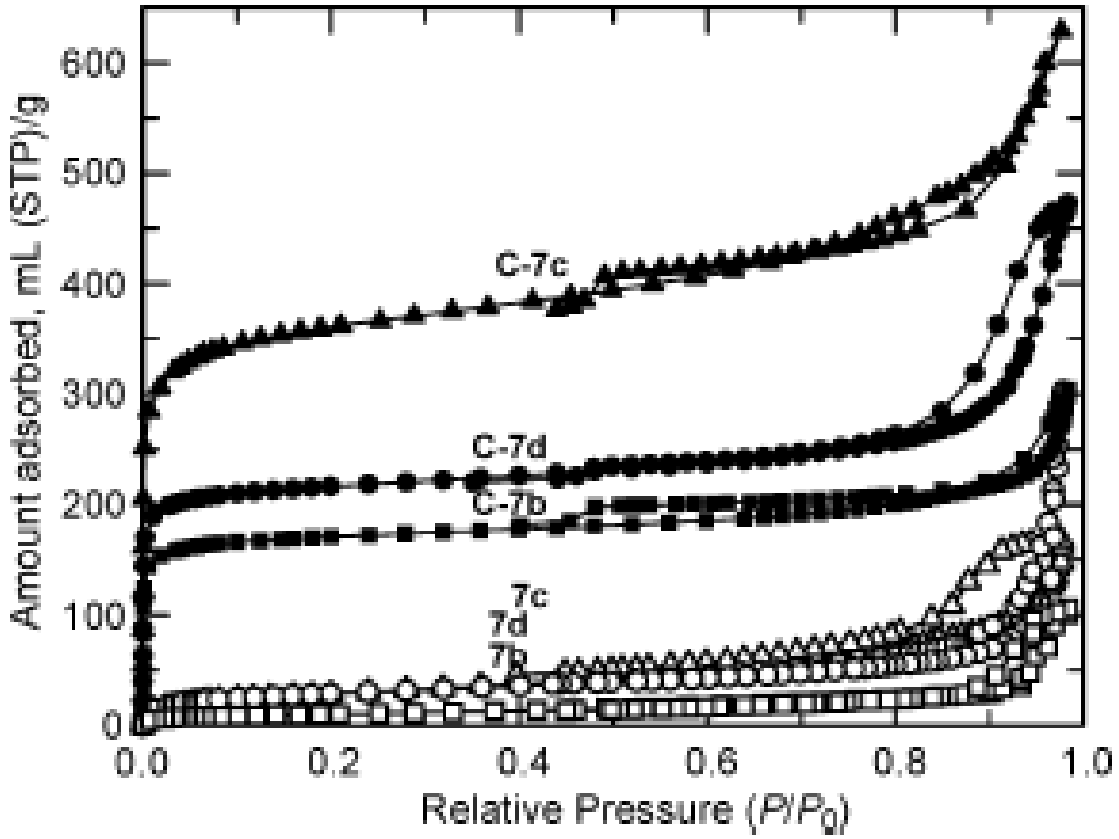
N_2 adsorption–desorption isotherms of the mesoporous coordination polymers and their carbonised samples

K_3**7**=





7b = K_3**7** + $Cu(OAc)_2$ in dioxane S_{BET}= 37 m^2/g **C7b** S_{BET}= 584 m^2/g

7c = K_3**7** +$Cu(OAc)_2$ in MeOH 105 carbonization **C7c** 1250

7d = K_3**7** + $CuCl_2 \cdot 2H_2O$ in MeOH 104 **C7d** 736

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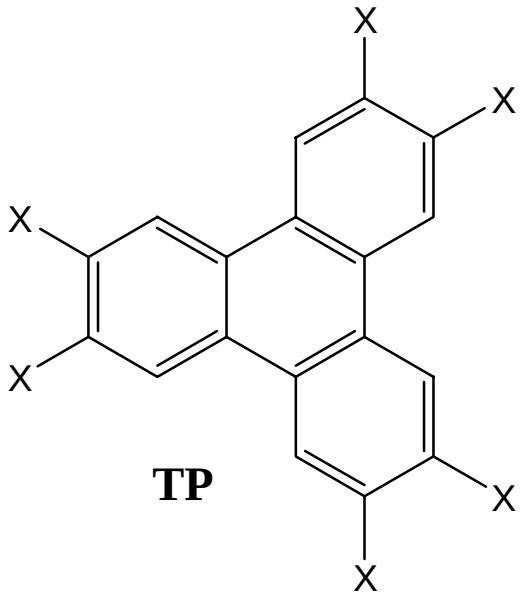
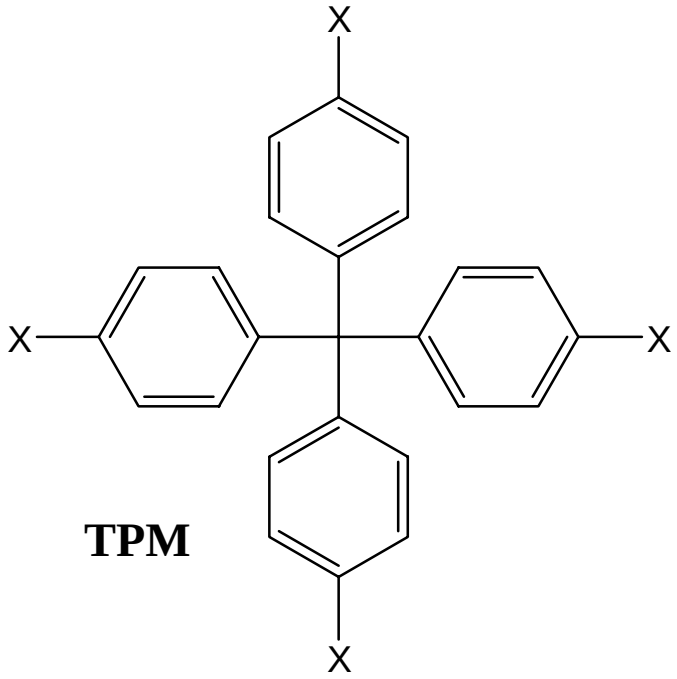
Organic linkers having triphenylene(TP) and tetraphenylmethane(TPM) structures



TP



TPM

TP(X=OH)，TPM (X=COCH2Br)，TPM (X=COCl)

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Summary of the surface parameters of COF and carbonized COF

Organic Linker	Connectors	Network material			C Yield %	Carbonized material		
		Yield %	S_{BET} m^2/g	V_{total} ml/g		S_{BET} m^2/g	V_{total} ml/g	V_{meso}/V_{total} %
TP(OH)	$Ph(CH_2Cl)_2$	85	2	0.07	56	585	0.56	34
TP(OH)	$BrCH_2C{\equiv}CCH_2Br$	70	220	0.36	57	480	0.29	20
TPM(CH_2COCl)	$Ph(NH_2)_2$	80	183	0.58	40	600	0.53	22
TPM($COCH_2Br$)	$HOCH_2C{\equiv}CCH_2OH$	86	3	0.16	55	782	0.51	28
TPM($COCH_2Br$)	$Ph(COOK)_3$	90	42	0.12	40	798	0.81	44

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Summary and Conclusions

(1)Pyrolytic conversion of structured poly(*m*-phenylenebutadiynylene)s **P*m*PBs** to porous C

Structuration→ Increase external surface→ high specific surface area + mesoporosity

(2)Pyrolytic conversion of structured lignin-cellulose composites to porous C.

The soluble C(C1,C2) showed good carbonization yields. The L-C composites have a good processability to make thin films and particles. The structuration results in increase of S.

(3)Pyrolytic conversion of MOFs and COFs to porous C

The organic linkers showed high fixation of C on the pyrolysis. The network materials can be converted to microporous C

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