第19回建材情報交流会

平成18年11月22日

ナノ技術等を用いた最新防汚技術
Ⅴ　サスティナブル建築　Part-II

高分子材料の撥水化技術とその可能性

神戸大学工学部
応用化学科
西　野　孝
tnishino@kobe-u.ac.jp

高分子表面・界面 ⟷ Bulk

高強度・耐熱性・・・

接着剤・複合材料・フィルム・
繊維・バイオマテリアル・コーティング・・・

バルク特性 保持

表面改質

疎水性

撥水性
- ●物理的～荒れ
- ●化学的～

表面自由エネルギー；低

親水性

極性官能基の導入
- ●湿式
- ●乾式～プラズマ

剥離・耐水性（撥水・撥油）・防汚染・生体親和性

表面荒れ性

フラクタル表面
→ 撥水･撥油表面

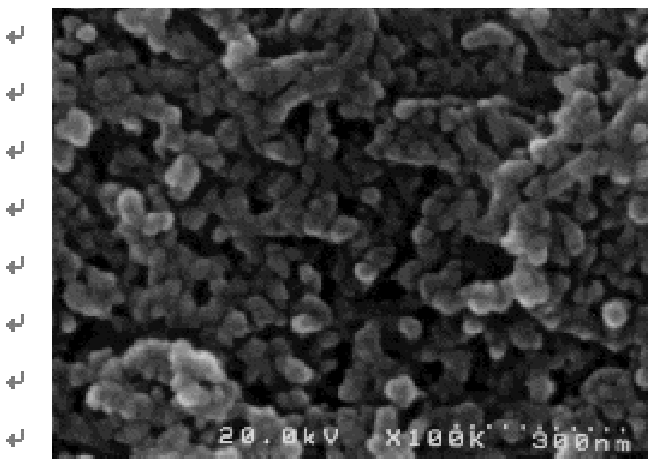
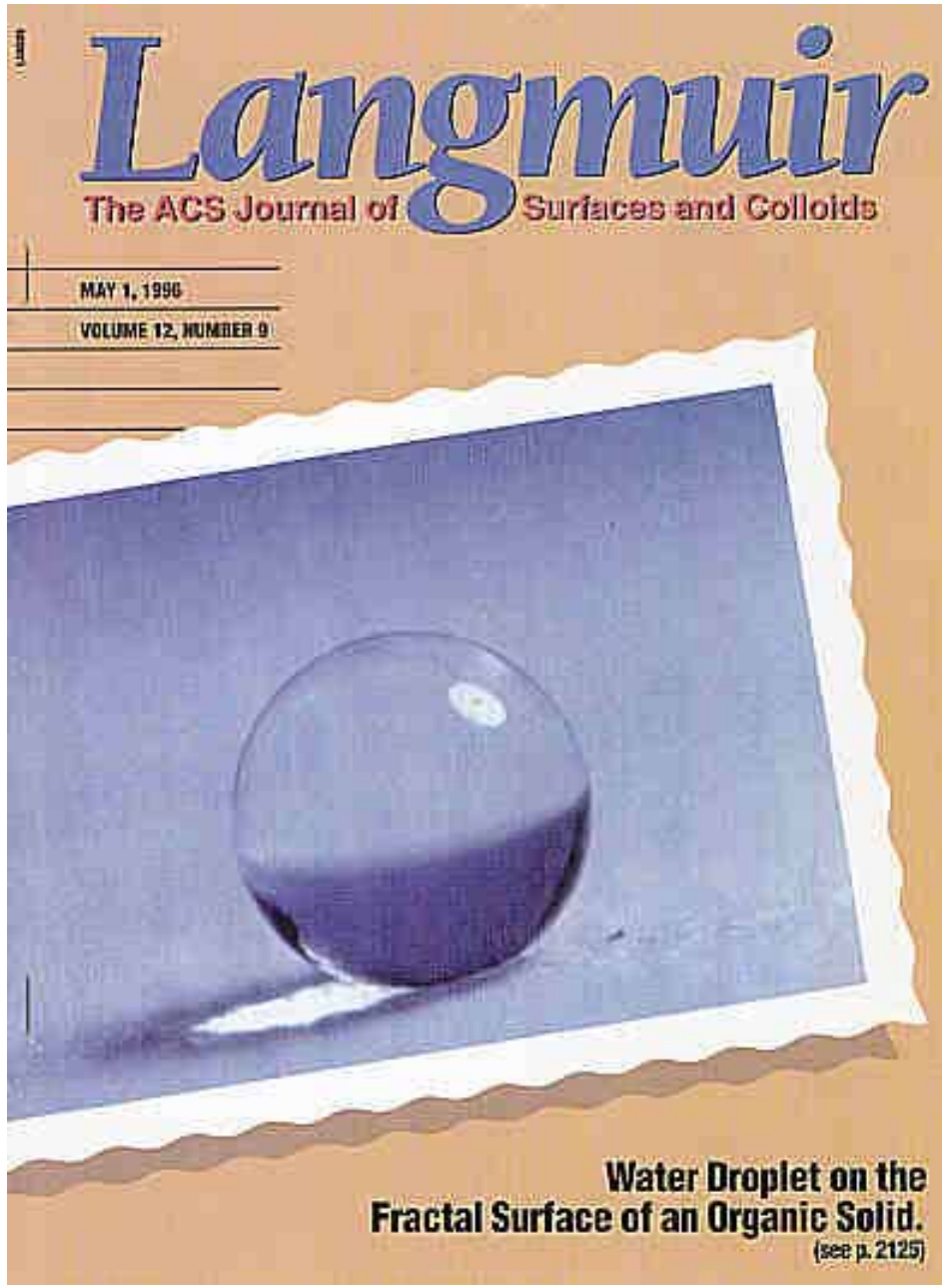


図１:陽極酸化後のアルミニウム表面

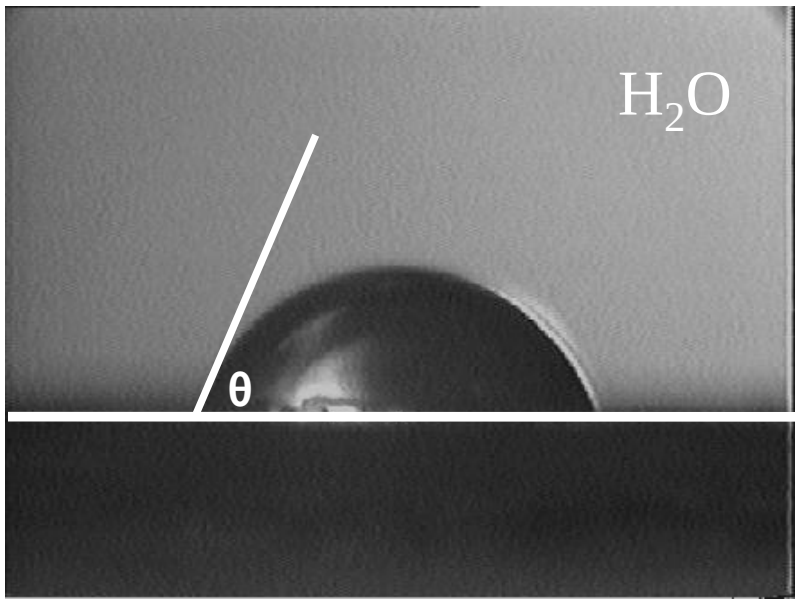


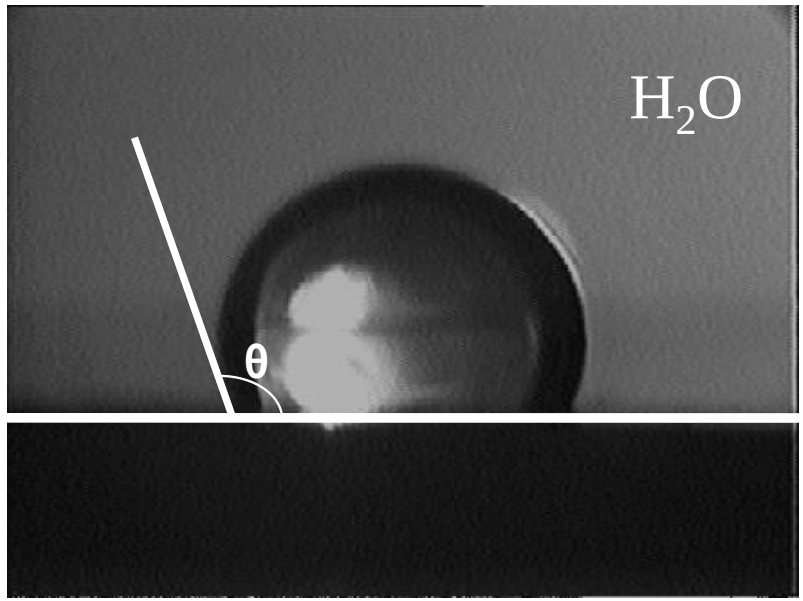
鄭･渡辺, 化学, 46, 477 (1991)

T.Onda, S.Shibuichi, N.Satoh, K.Tsujii,
Langmuir, 12, 2126 (1996).

高分子の表面性質

動的接触角 (Dynamic Contact Angle)





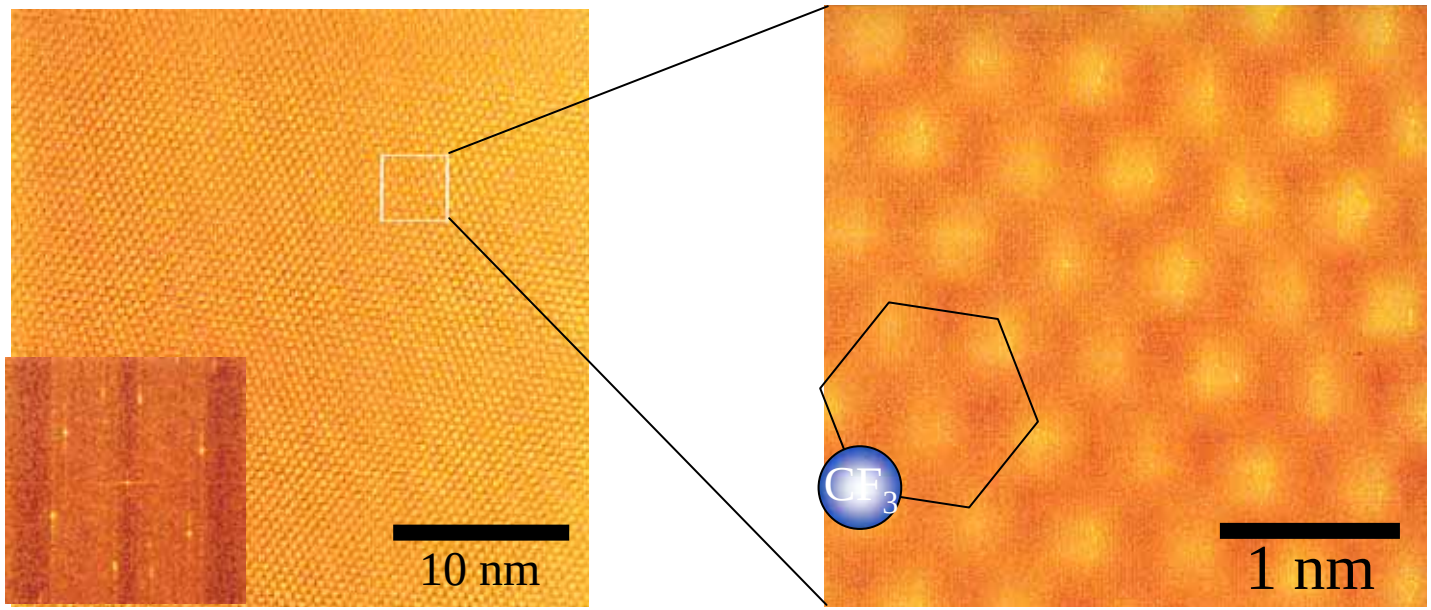
低 ——— 水との接触角 ——— 高

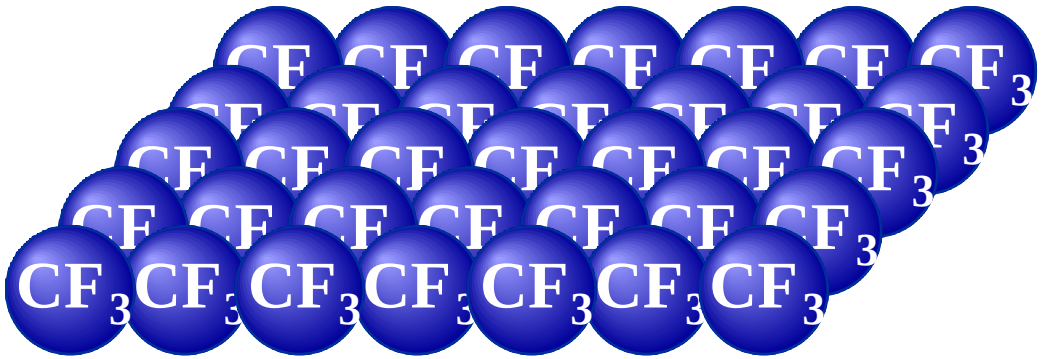
濡れる　　撥く

親水性　　疎水性 (撥水性)

高 —— 表面自由エネルギー ——低

Perfluoroeicosane ($CF_3(CF_2)_{18}CF_3$) **Vapor Deposition**





-CF_3 Regular Aligned
Hexagonal Closest Packing

$\theta = 119^{\circ}$ (water)

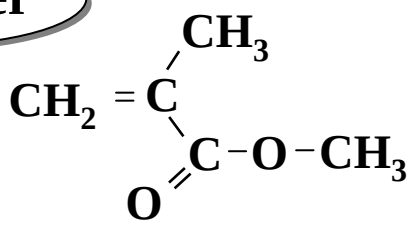
$\gamma = 6.7$ mJ / m^2

The Lowest Surface Energy

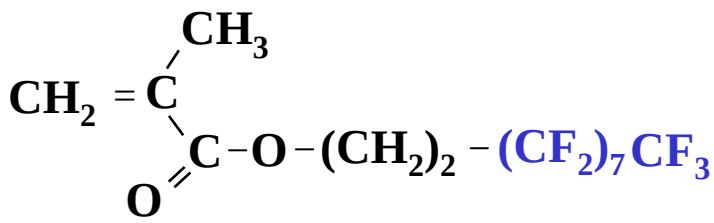
T. Nishino *et al.*, *Langmuir*, 15 (1999) 4321

Synthesis

Monomer



Methyl methacrylate (MMA)



2-perfluorooctylethyl methacrylate (PFEMA)

Living Anionic Copolymerization

s-BuLi, THF, -78 ° C

Radical Copolymerization

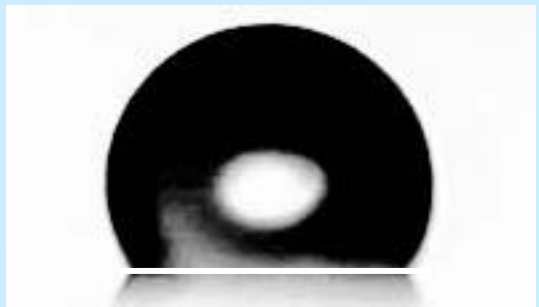
AIBN, MIBK, 70 ° C, 24h

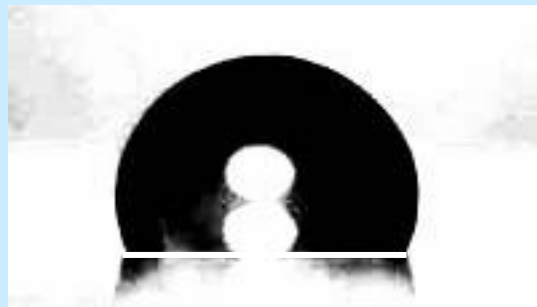
Copolymers	Mn[a)]	Mw/Mn[a)]	PFEMA content[b)]
Diblock	11900	1.08	15.2
Random	12800	1.51	17.6

a) : determined by GPC b) : determined by ^{1}H-NMR (mol%)

Sequence Control

T.Nishino, Y.Urushihara, M.Meguro, K.Nakamae
J.Colloid and Interface Sci., 279, 364 (2004).



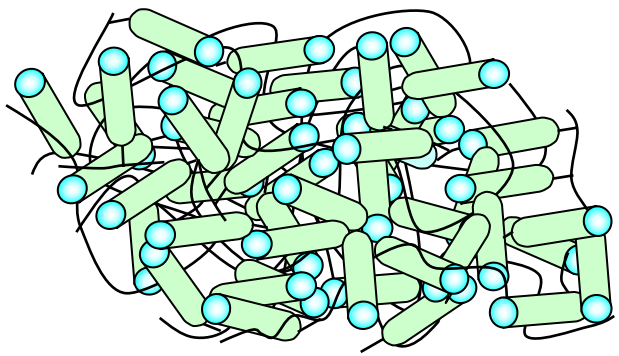


Diblock **Random**

Polymer	Water (degree)	CH_2I_2 (degree)	Surface free energy (mJ/m^2)
Diblock	120	103	7.8
Random	93	65	26.4
PTFE	98	70	18.0
The Lowest	119	107	6.7

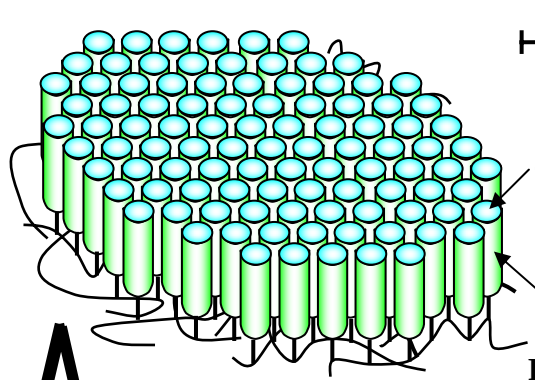
Low surface free energy

Random copolymer



- No self-assembly

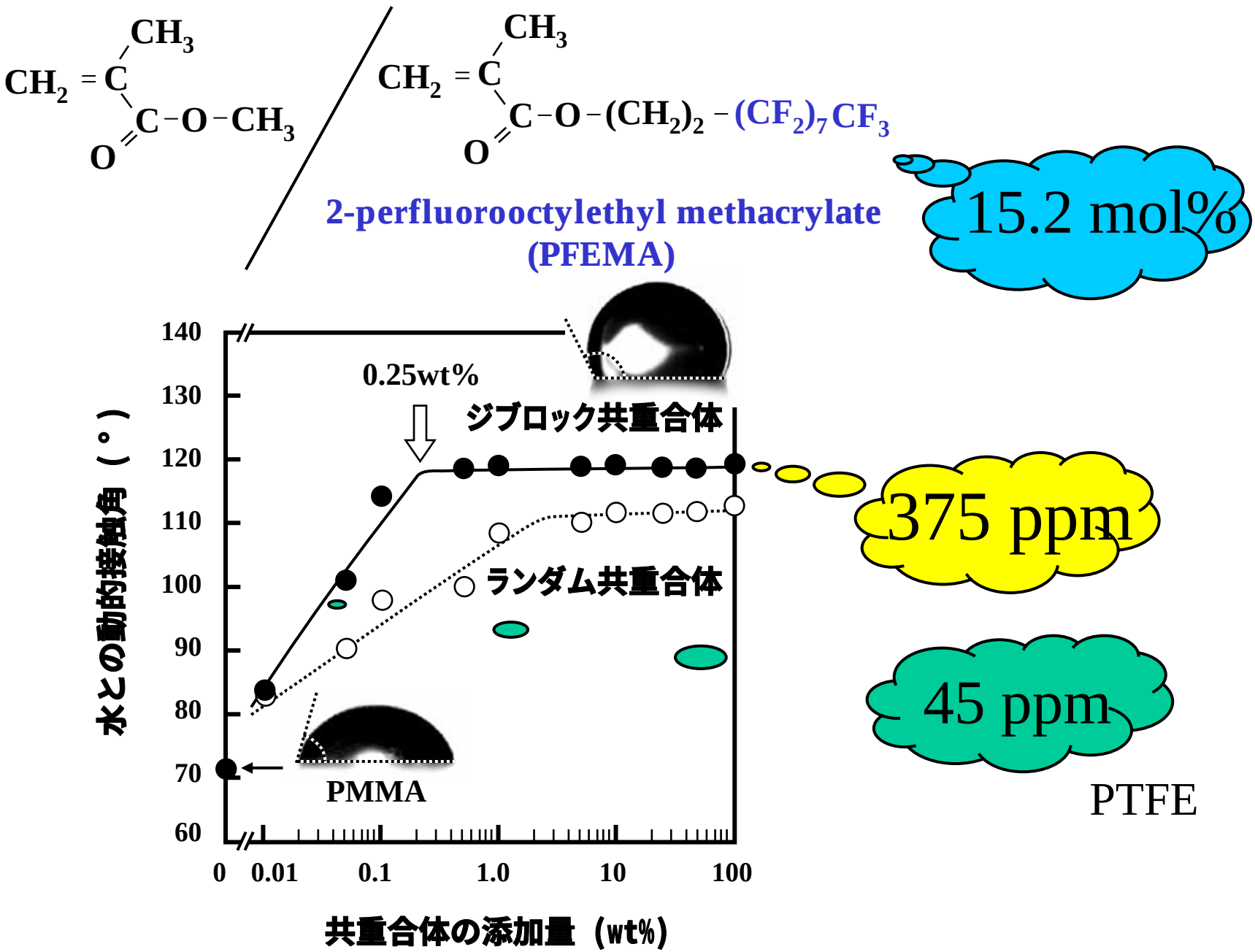
Diblock copolymer



7.8 mJ /cm^2

ESCA
FTIR RAS
GIXD

Stable -CF_3 surface

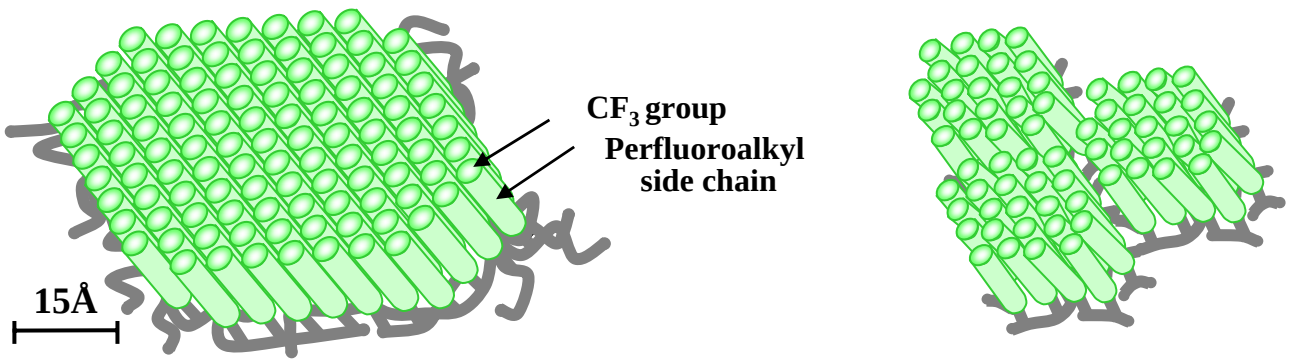

CH3
CH2 = C
C – O – CH3
O
CH3
CH2 = C
C – O – (CH2)2 – (CF2)7 CF3
O
2-perfluorooctylethyl methacrylate
(PFEMA)
15.2 mol%
140
130
120
110
100
90
80
70
60
水との動的接触角（°）
0.25wt%
ジブロック共重合体
ランダム共重合体
PMMA
375 ppm
45 ppm
PTFE
0
0.01
0.1
1.0
10
100
共重合体の添加量（wt%）

• *Diblock copolymer vs. Homopolymer*

Table. Dynamic contact angles and the surface free energy γ_s of diblock copolymer and homopolymer.

Polymer	PFEMA content (mol%)	Solvent	Water (degree)	CH_2I_2 (degree)	γ_s (mJ/m^2)
Diblock	15.2	Chloroform	120	103	7.8 ± 0.2
Homo	100	$CF_3CF_2CHCl_2$	118	100	8.5 ± 0.4

Self-assembled structure at surface



Diblock (chloroform)

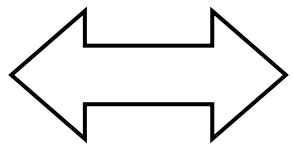
Homopolymer ($CF_3CF_2CHCl_2$)

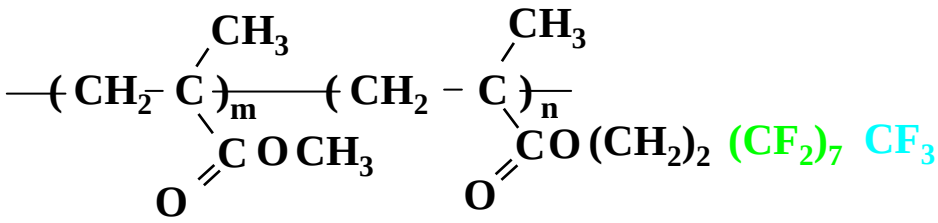
Cast solvent effect

T.Nishino, Y.Urushihara, M.Meguro, K.Nakamae
J.Colloid and Interface Sci., vol.283, pp.533-538 (2005).

Table. Surface free energies of the Diblock copolymer films cast and spin-coated from various solutions.

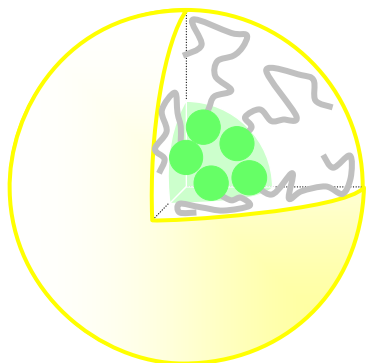
Solvent	γ_s (mJ/m^2)	
	Cast film	Spin-coated film
Chloroform	7.8	27.5
Trichloroethylene	8.1	28.4
Ethyl acetate	9.9	27.9
THF	11.7	28.0
MEK	11.8	27.8
Toluene	22.2	27.2
Benzene	23.0	27.7
HCFC-225	9.9	12.2
TFMB	10.8	12.4





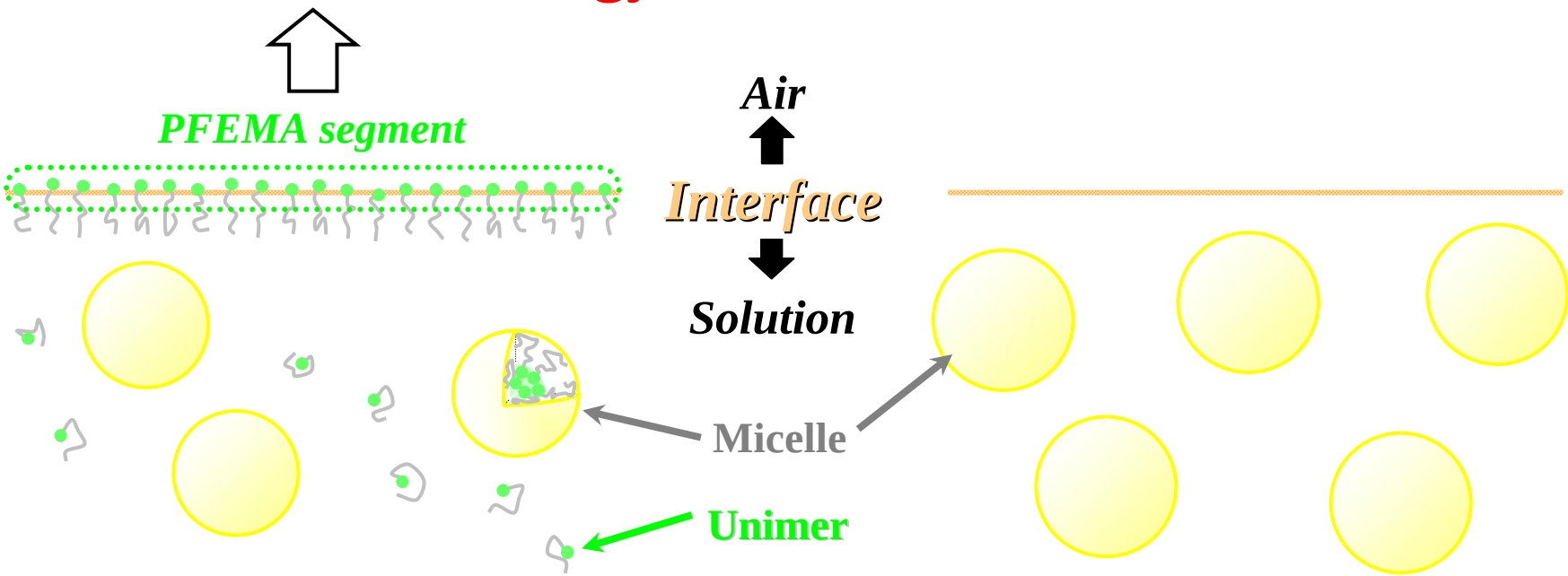
Solvent	Solubility	
	MMA segment	PFEMA segment
Chloroform	○	×
Trichloroethylene	○	×
Ethyl acetate	○	×
THF	○	×
MEK	○	×
Toluene	○	×
Benzene	○	×
HCFC-225	○	○
TFMB	○	○

Micelle



Model of Air/Solution Interface

Low surface free energy



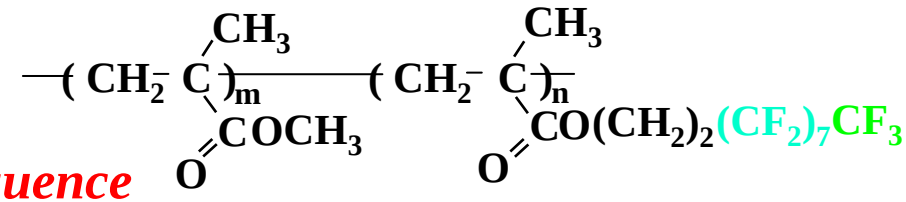
Chloroform

7.8 mJ/m^2

Toluene

22.2 mJ/m^2

Y.Urushihara, and T.Nishino, *Langmuir*, vol. 21, 2614-2618 (2005).



- ***Molecular sequence***
- ***Film-forming condition***
  - Cast solvent effect
  - Film-forming technique
- ***Annealing effect***

structure → Surface properties

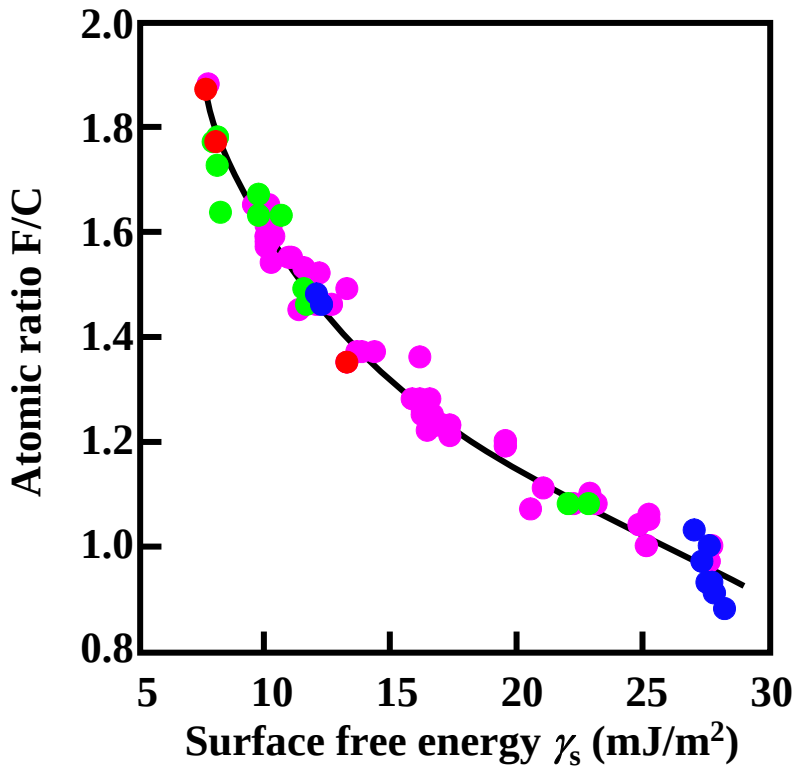


Fig. Relationship between the surface free energy and the atomic ratio F/C on the film surface of the polymethacrylate with perfluoroalkyl side chains

西野　孝, 科学と工業, 80**巻**, 512 (2006)

EPA is advised to increase estimate of PFOA's cancer risk

EPA's Science Advisory Board (SAB) is recommending that the agency deem perfluorooctanoic acid (PFOA) a "likely" human carcinogen. The scientific advisers endorsed a report at a Feb. 15 meeting that says the compound poses a greater risk than described in an EPA draft risk assessment of PFOA released in January 2005. That draft found only "suggestive evidence" that the compound poses a cancer risk (C&EN, Jan. 17, 2005, page 28). Before SAB approved the report, researchers from 3M, a former manufacturer of the substance, and DuPont, which has used PFOA for decades, argued against upgrading the classification of the chemical's cancer risk. They said the board's recommendation was largely based on a study linking PFOA to mammary gland tumors in rats. They cited an unpublished report reexamining that study and dismissing the cancer association. SAB members noted that much new information is emerging on the health effects of the chemical, and EPA will consider it as the agency crafts the final version of the PFOA risk assessment.

PFOS: 3M

$C_8F_{17}SO_3^-$

PFOA: Du Pont

$C_7F_{15}COOH$

↑

$C_8F_{17}CH_2CH_2OH$

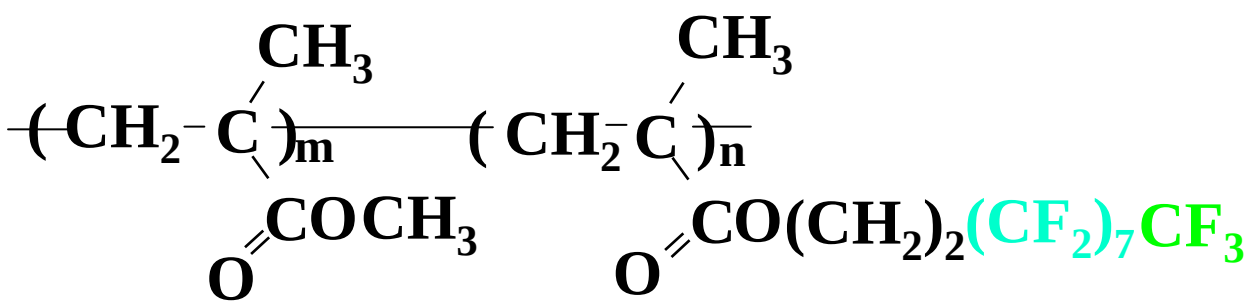
Chemical & Engineering News (Feb.20,2006) p.26

フッ素系高分子

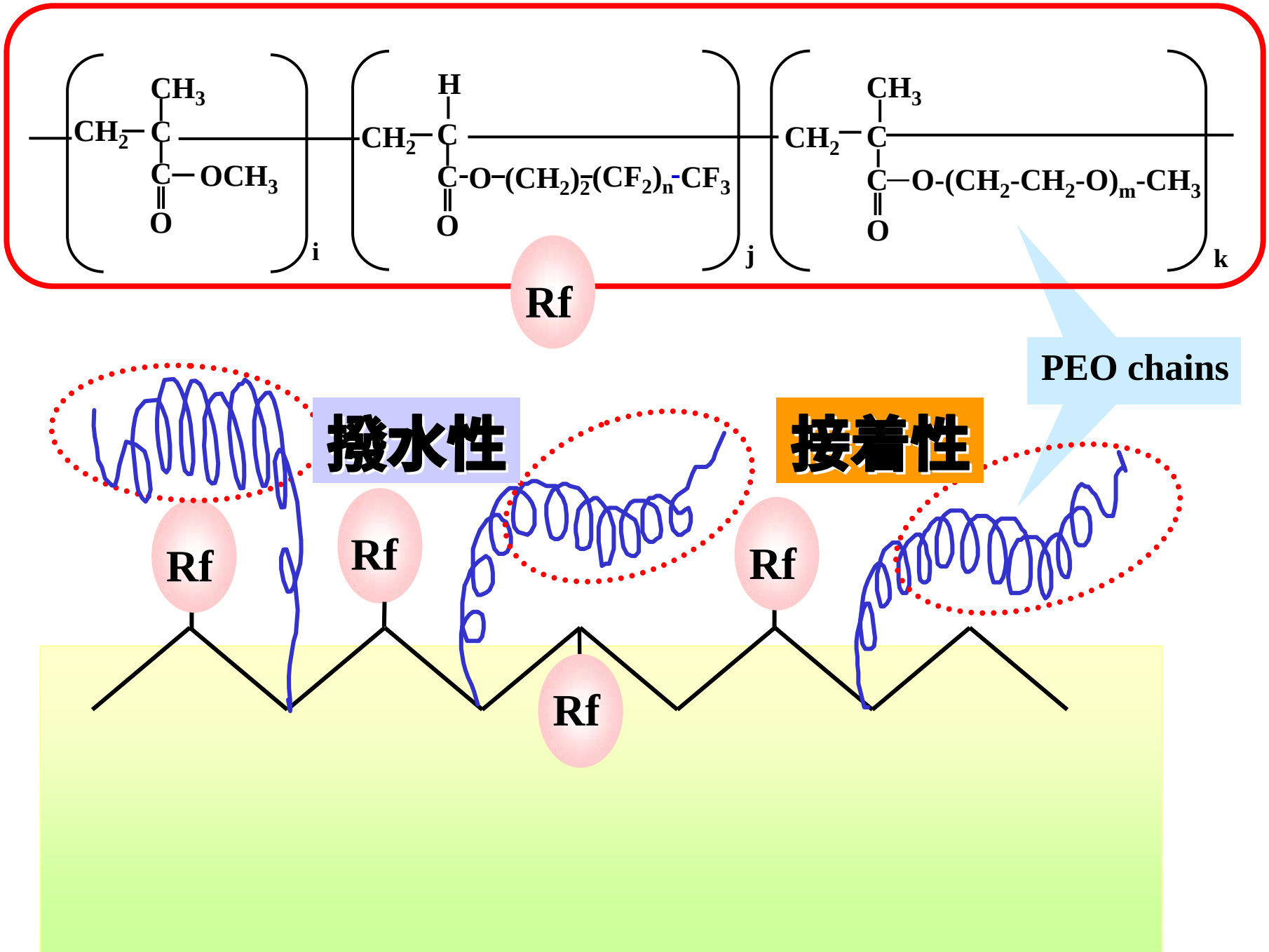
ポリテロラフルオロエチレン (PTFE)

- 撥水・撥油性
- 低接着性・剥離性
- 低摩擦性
- 低誘電率
- 耐溶剤性

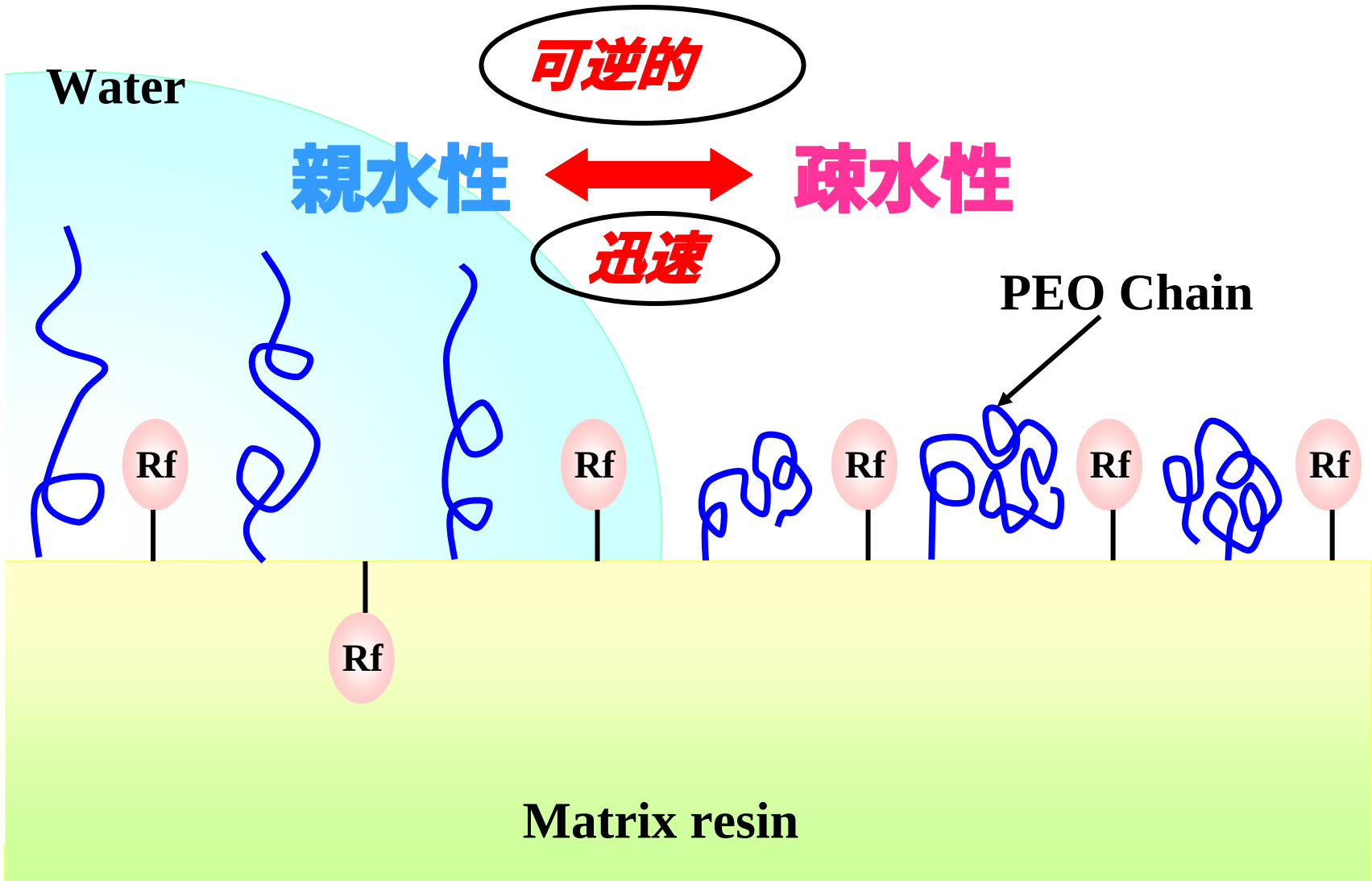
- 成型加工性
- 機械的強度
- 価格
- 生体蓄積性



高撥水性 ＋ 高接着性


Rf
PEO chains
撥水性
接着性
Rf
Rf
Rf
Rf

Environmental Response



Adhesive Test ～90 ° Peel Strength to Epoxy Resin

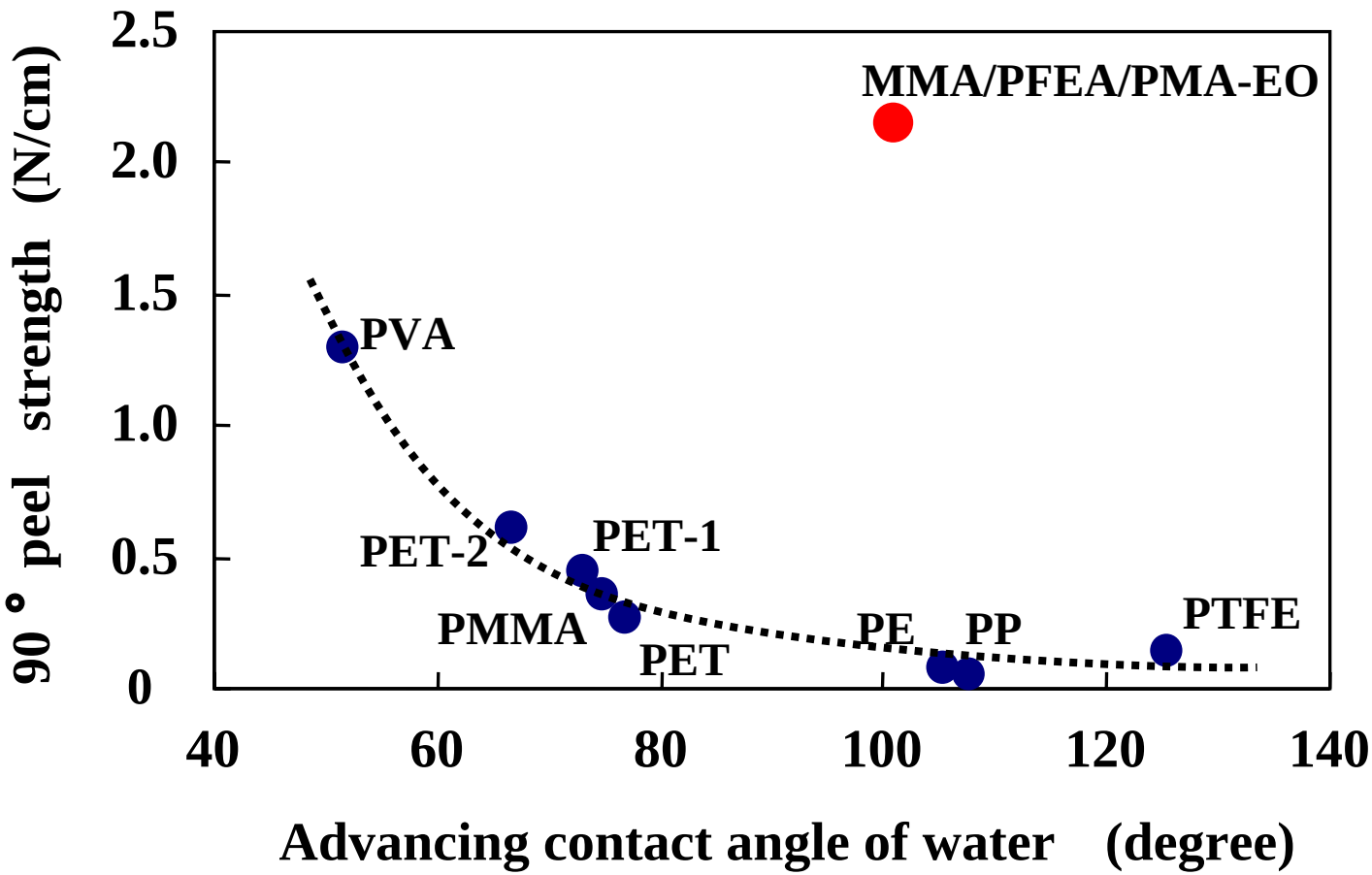
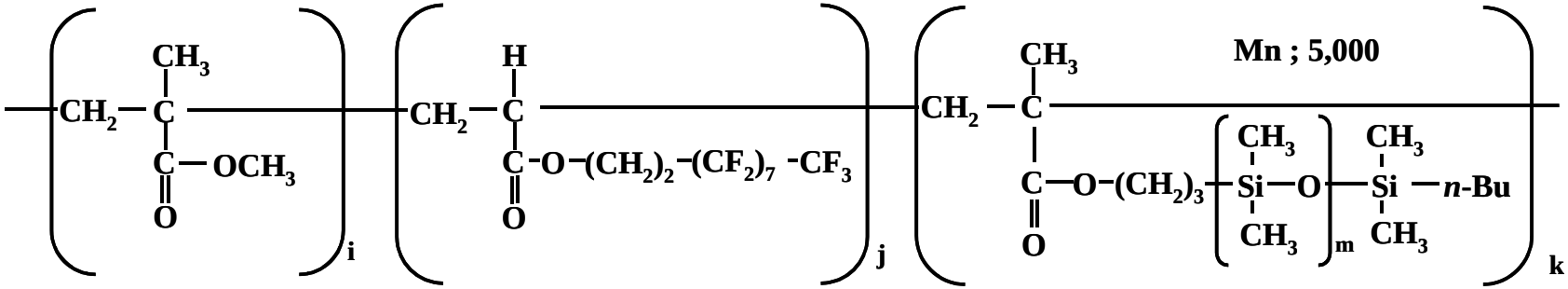
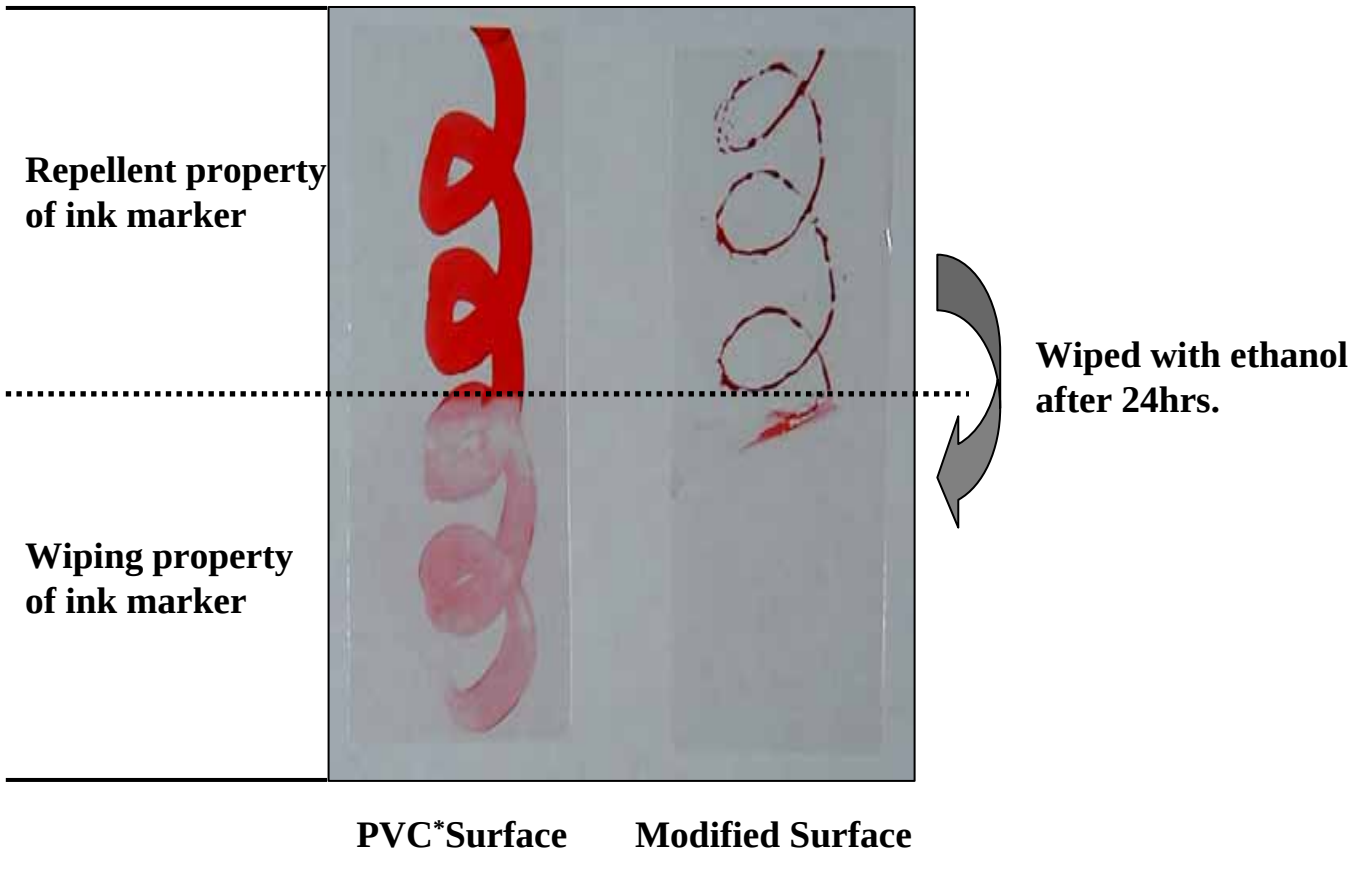


Fig. Relationship between 90 ° peel strength and the advancing contact angle of water on various polymers.





*PVC : polyvinylchloride