

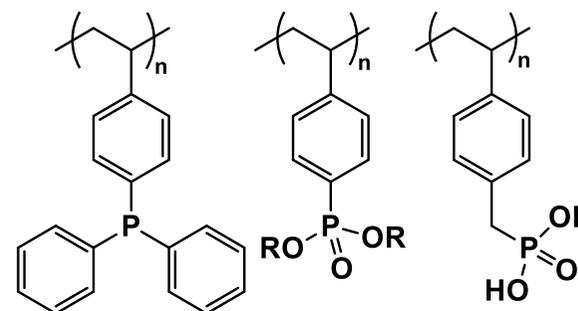
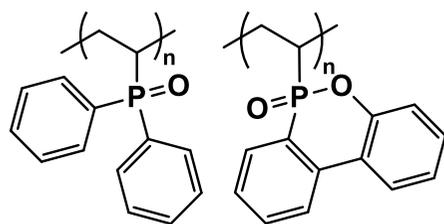
# 各種チオホスフィノ基を有するスチレンの重合挙動と ホスフィン含有ポリマー合成

反応有機化学分野

後藤 千怜

## 側鎖にリン官能基を含むポリマー

## 難燃性ポリスチレン



リン官能基を含むポリスチレンは  
ジフェニルホスフィノ基型、リン酸エステル型に限られる

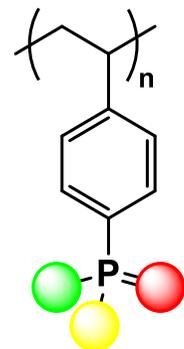
Li-Biao Han *et al.*, WO 2010098047 A1.

G. David, C. Negrell-Guirao, F. Iftene, B. Boutevin and K. Chougrani, *Polym. Chem.*, **2012**,3, 265.

R. Liu, C. Lin, Y. Zou, W. Sun, Y. Yang, C. Wei, J. Zhong, L. Shen, *Appl. Polym. Mater.* **2024**, 6, 11633.

難燃性

接着性

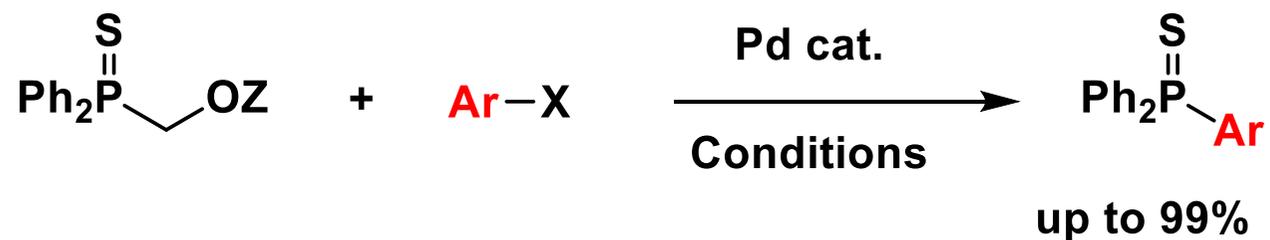


リン官能化PS

金属  
スカベンジャー

金属触媒  
の高分子  
配位子

## • P-Cクロスカップリング反応



X = I, Br, OTf

**Conditions**

DBU, Toluene (Z = H)

NaOEt, THF (Z = Bz)

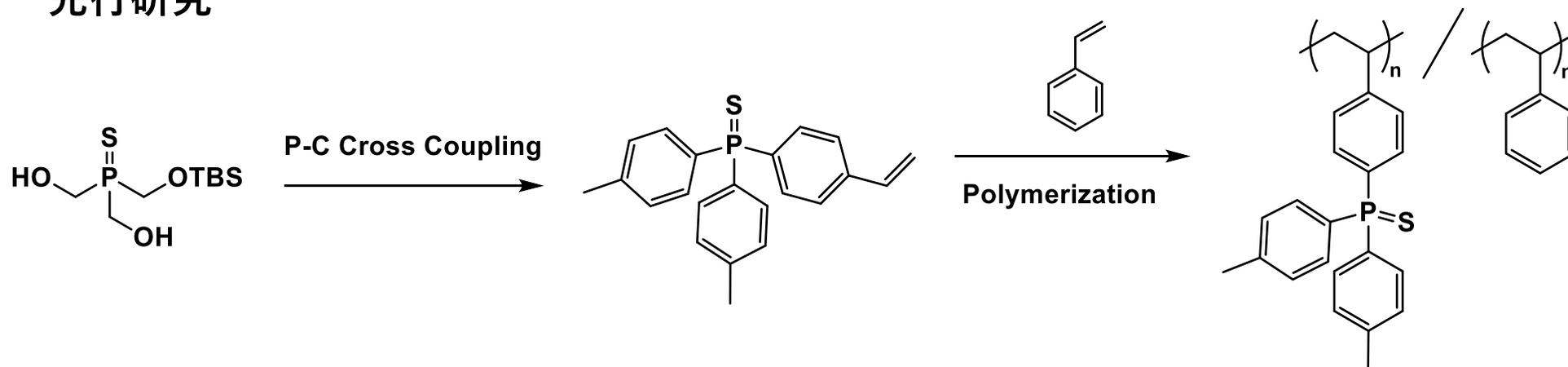
CsF, THF (Z = TBS)

M. Hayashi, T. Matsuura, I. Tanaka, H. Ohta, and Y. Watanabe, *Org. Lett.* **2013**, *15*, 628.  
H. Ohta, Q. Xue, M. Hayashi, *Eur. J. Org. Chem.* **2018**, *6*, 735.

# 研究目的

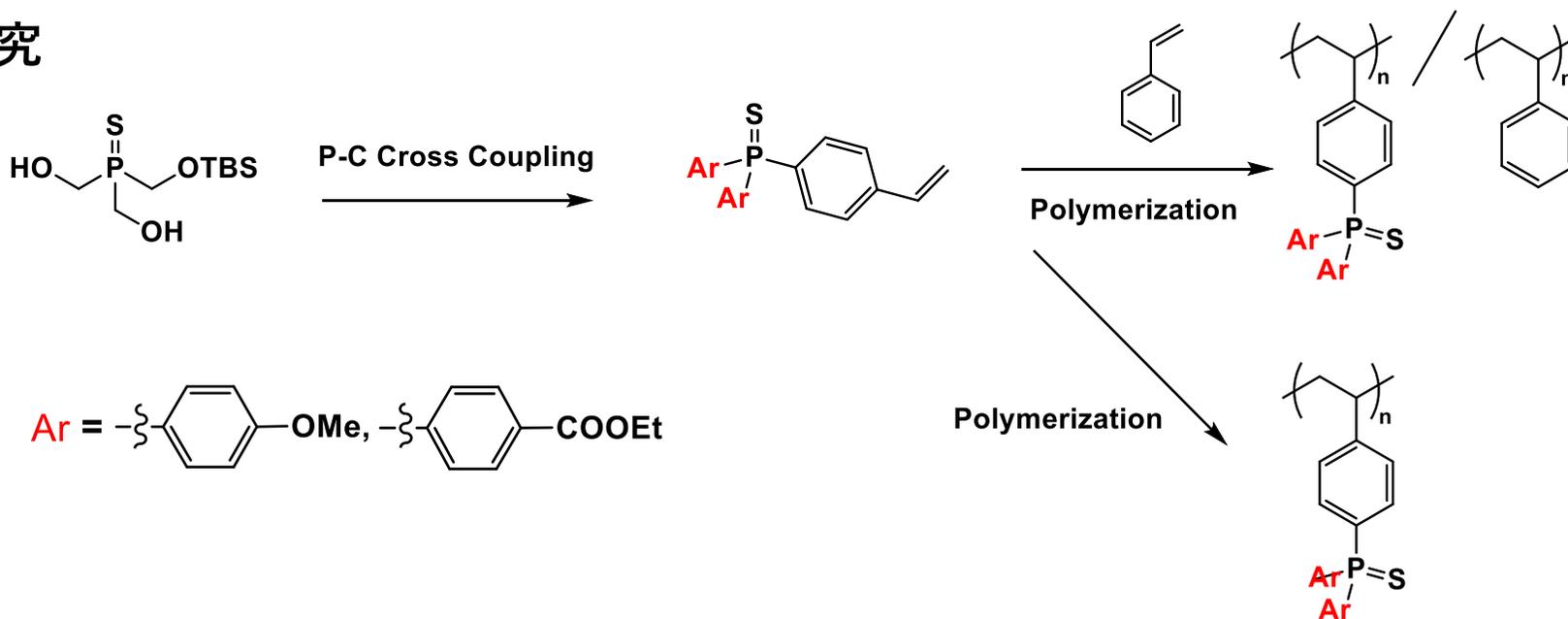
4

## 先行研究



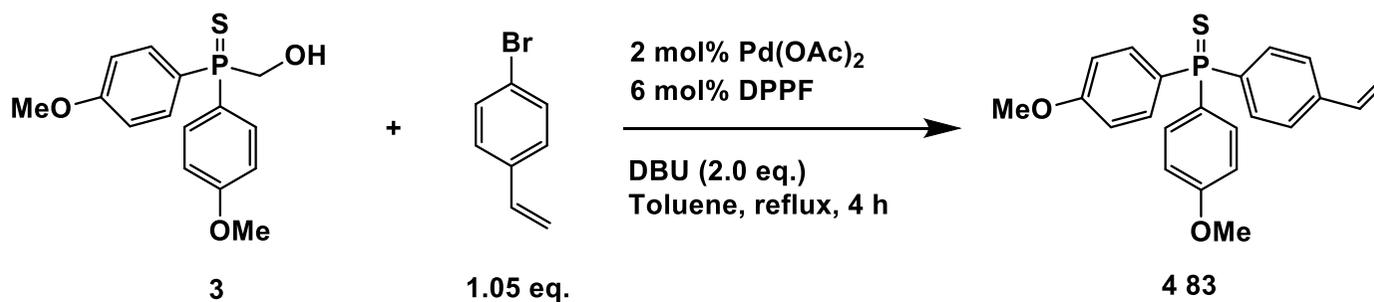
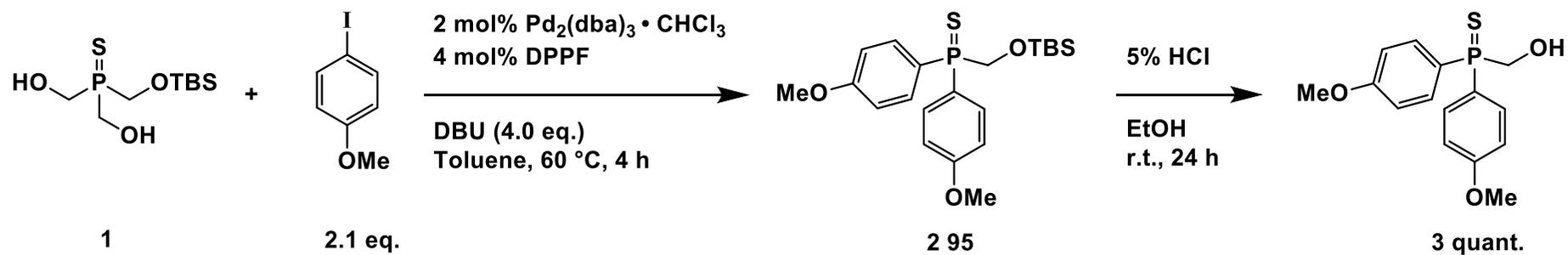
E. Okazaki, M. Hayashi, H. Ohta, *CSJ 105th Annual Meeting (2024)*, 2am-08

## 本研究

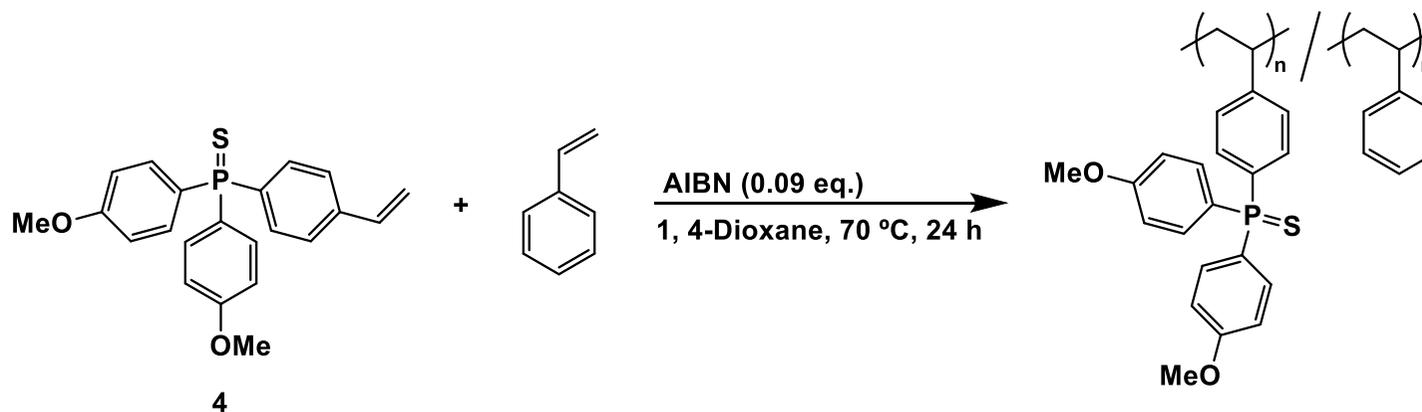


# モノマー合成

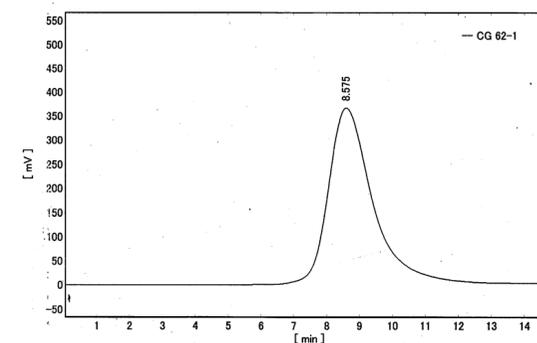
5



# スチレン当量検討

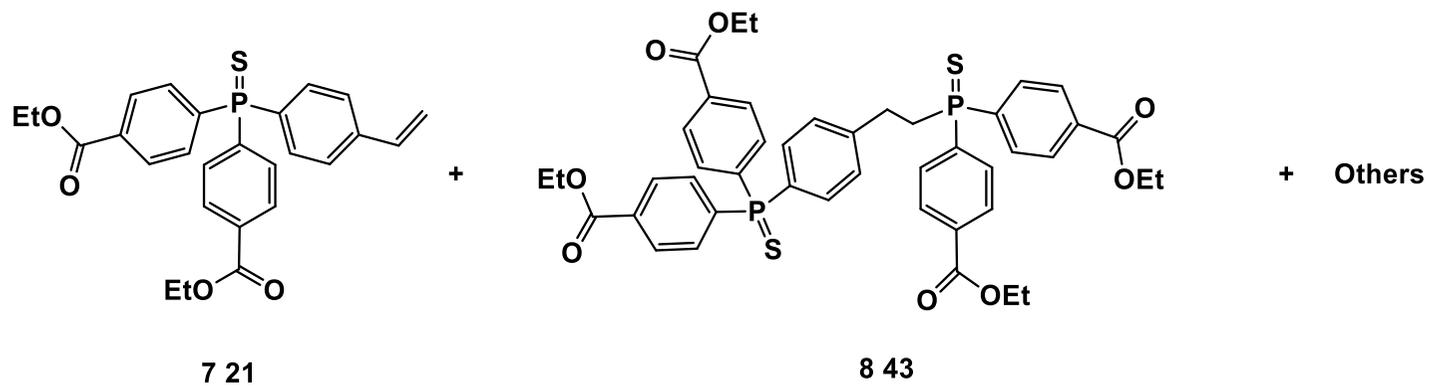
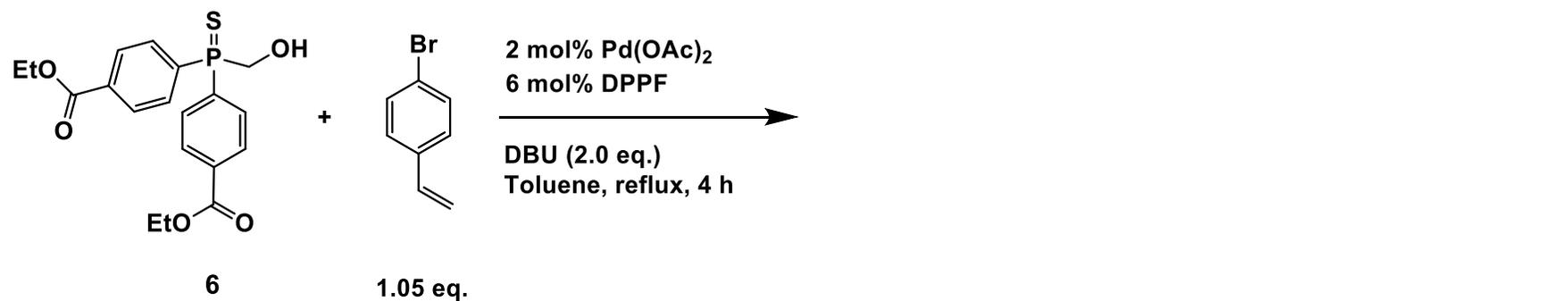
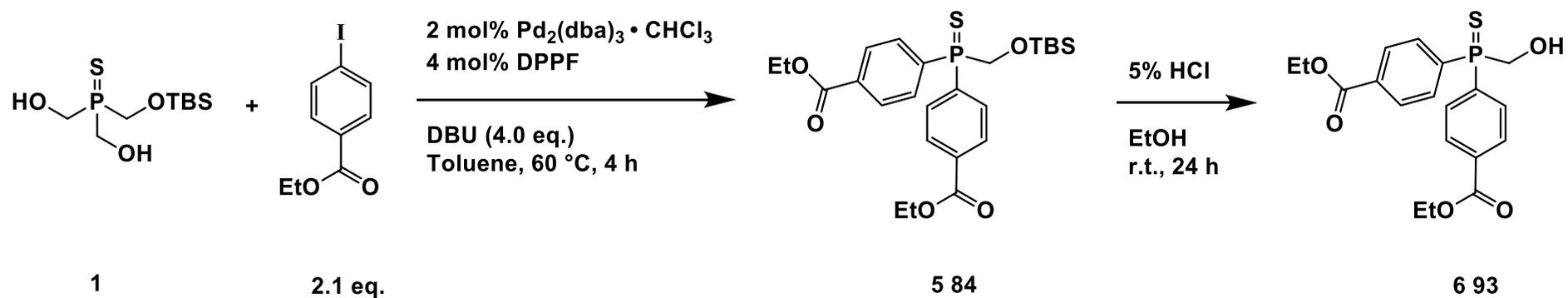


Entry	Styrene[eq.]	Conv.[%]	スチレン含有率 [%]	Mn	Mw / Mn
1	0	82	0	1900	2.0
2	0.5	83	22	2700	2.0
3	1	85	37	3200	2.3
4	2	85	56	3000	1.9
5	5	89	77	2300	1.9

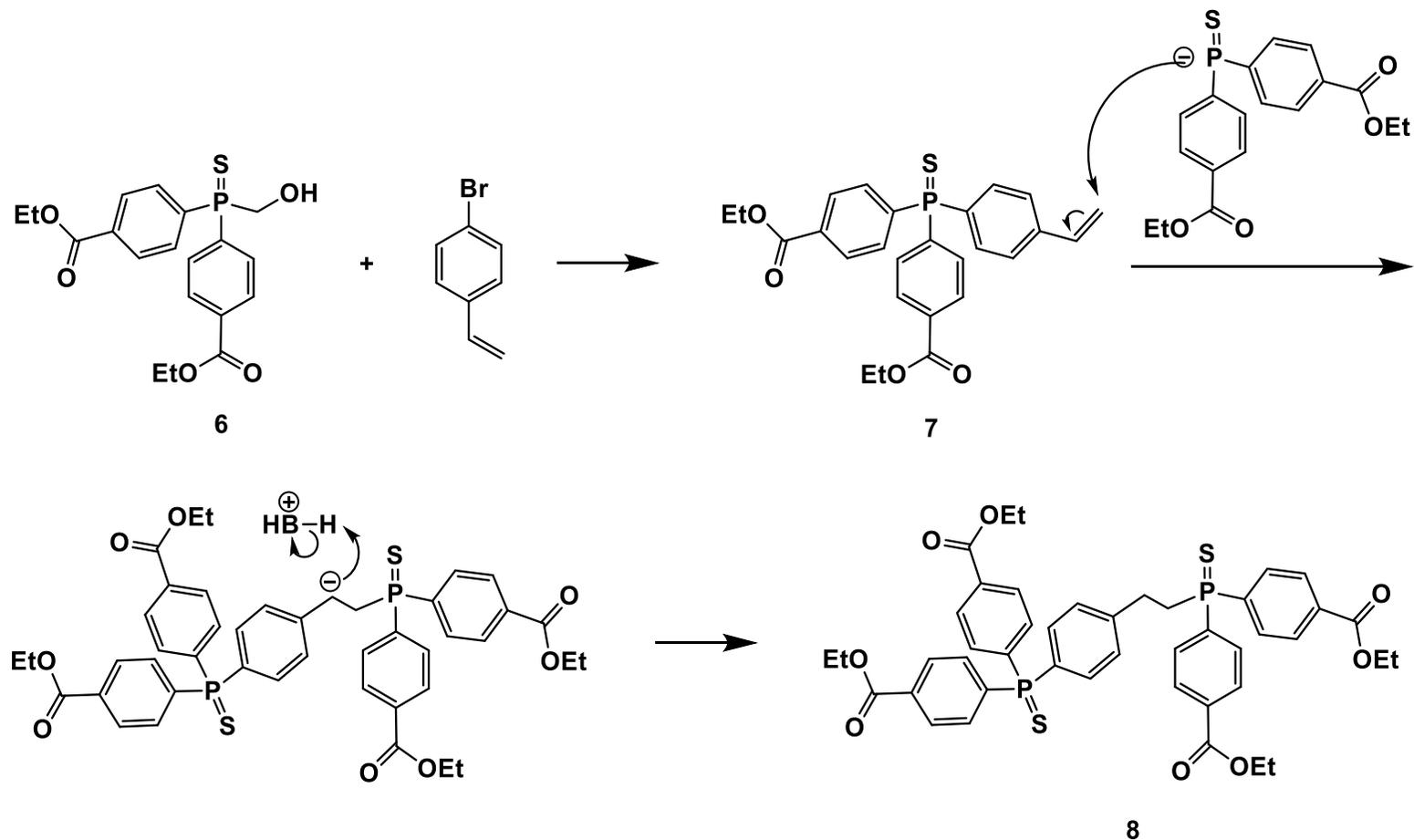


Entry 3 分析GPC

# モノマー合成

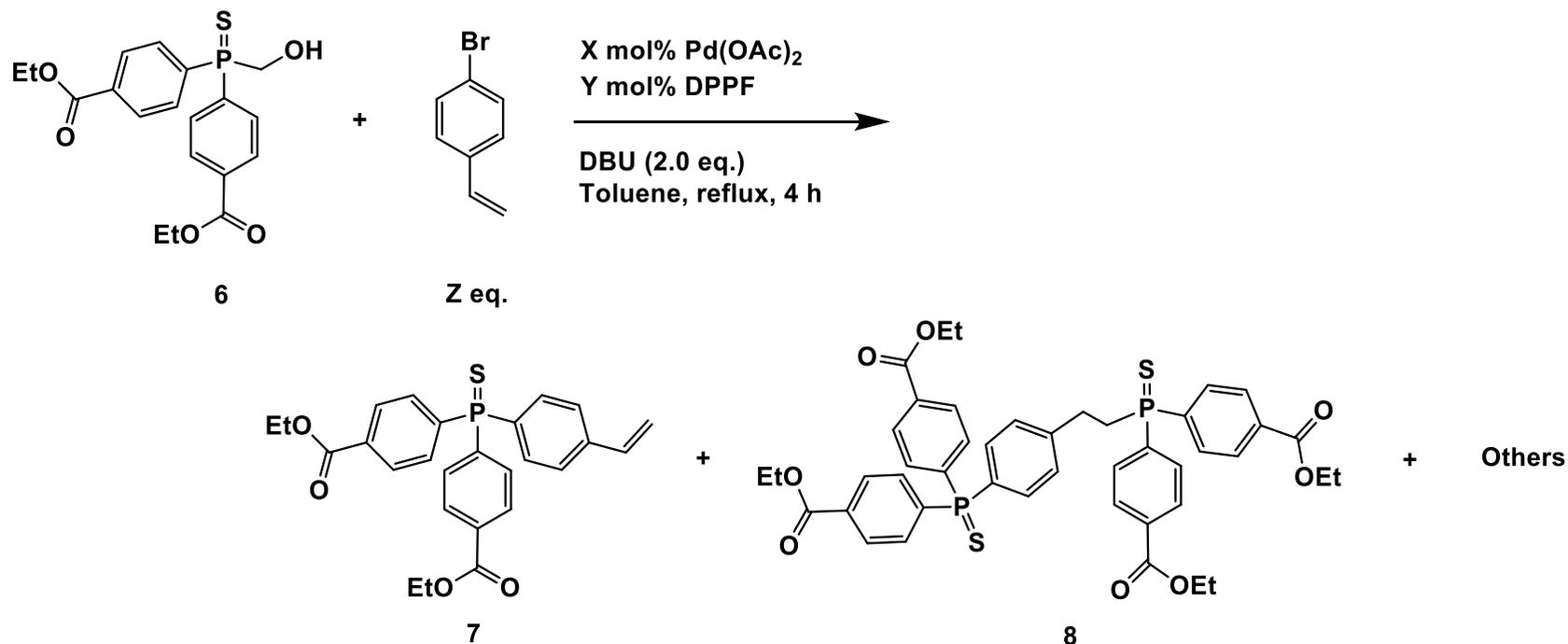


# 副生成物の推定生成機構



# モノマー合成検討

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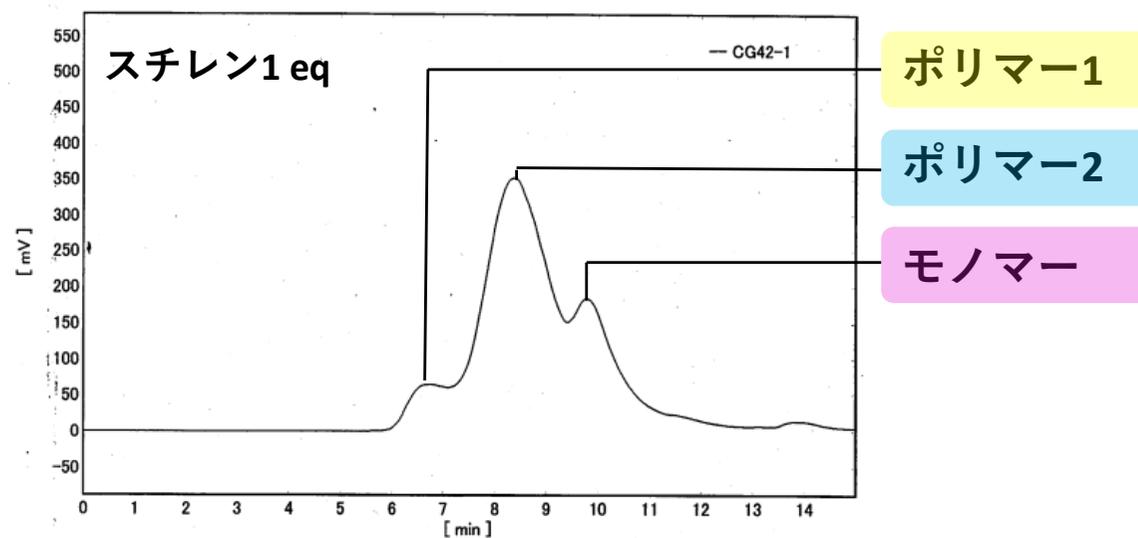
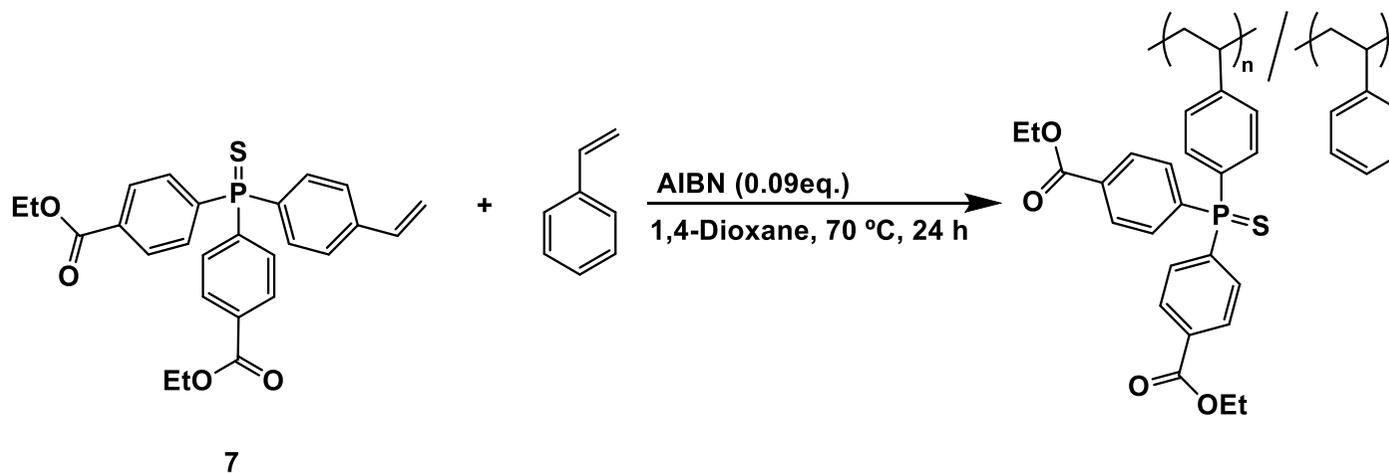
Entry	X	Y	Z	Result / % <sup>a</sup>		
				7	8	Others
1	2	6	1.05	46 (21) <sup>b</sup>	51 (43) <sup>b</sup>	3
2	4	12	1.05	30	50	20
3	2	6	2.1	100 (87) <sup>b</sup>	0	0

a) Yield was calculated based on <sup>31</sup>P NMR spectra.

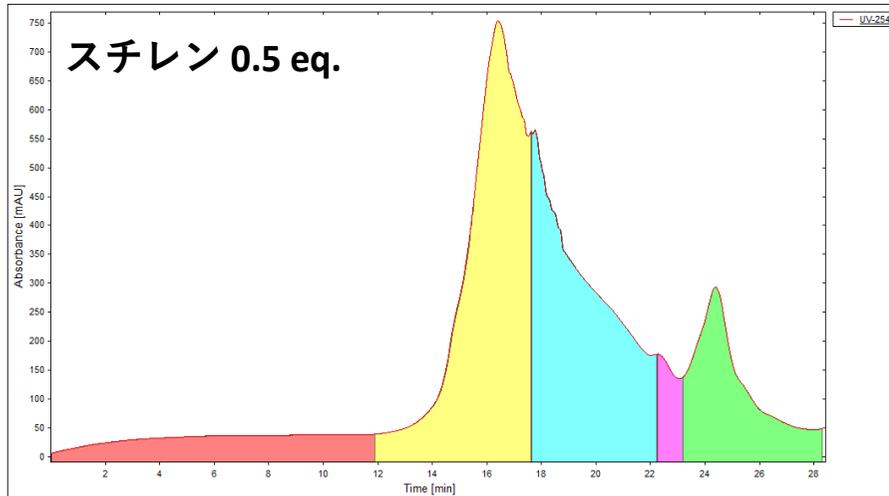
b) Isolated Yield

# スチレンとのラジカル共重合

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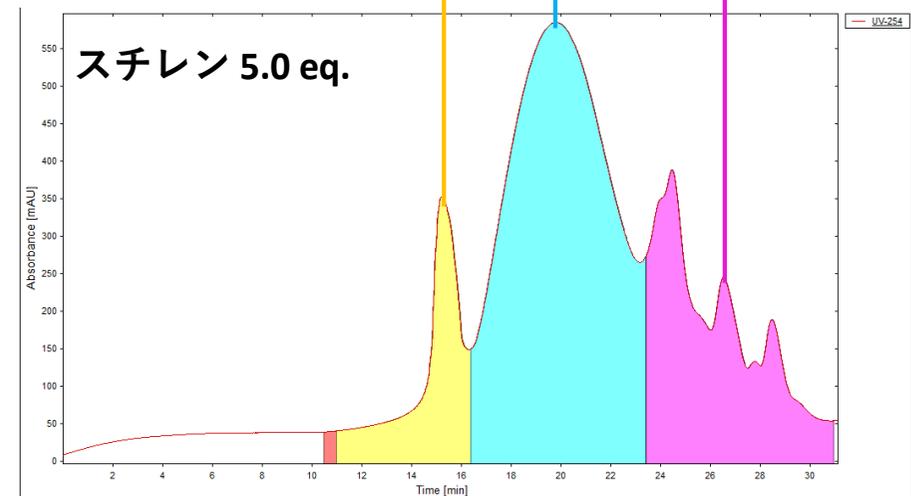
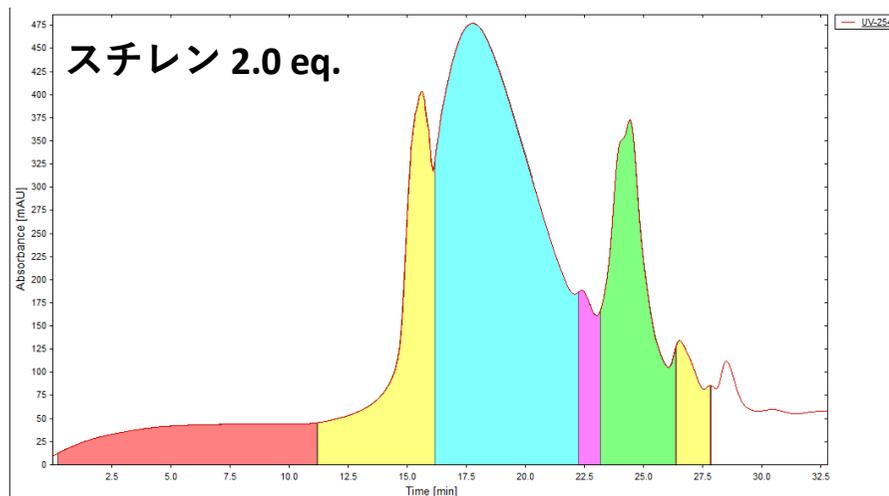
分析GPC



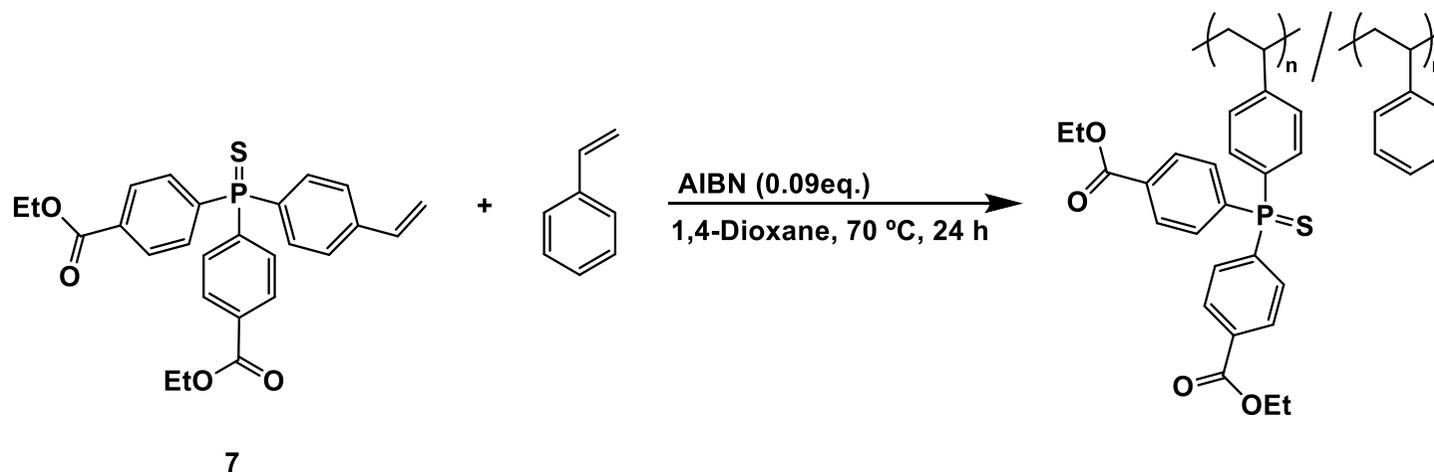
Fraction A

Fraction B

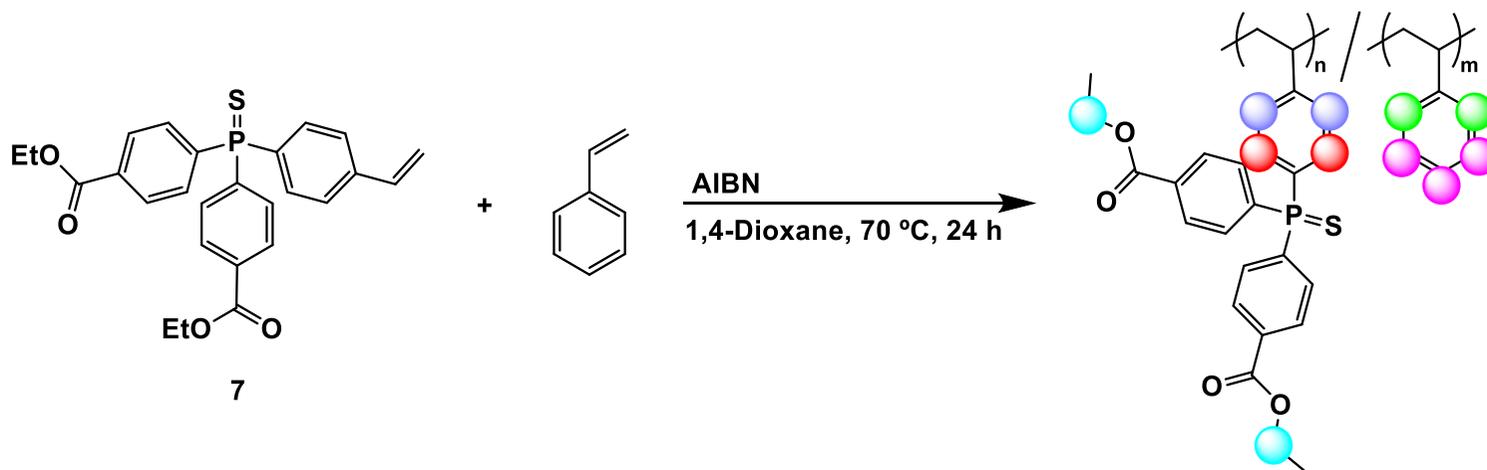
Fraction C  
(モノマー)



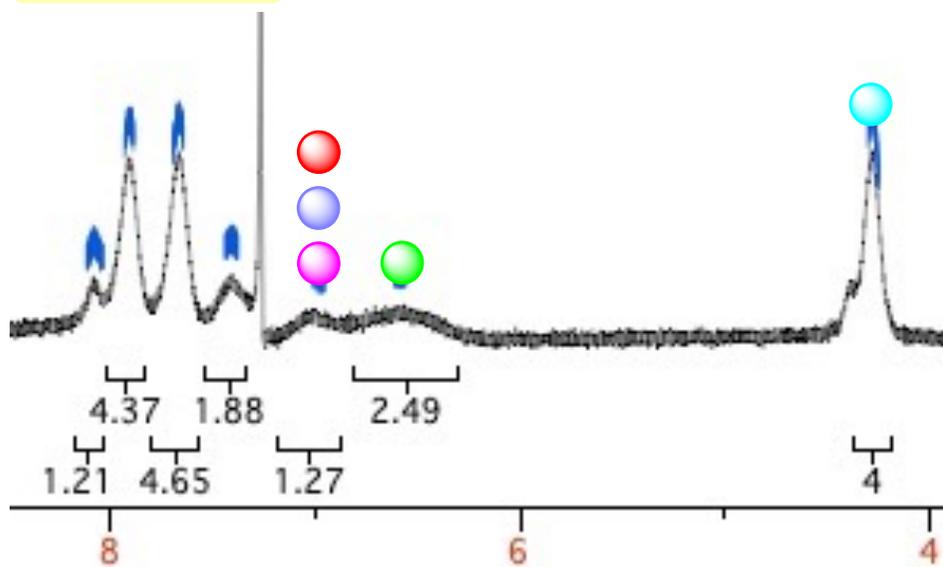
# スチレン当量検討



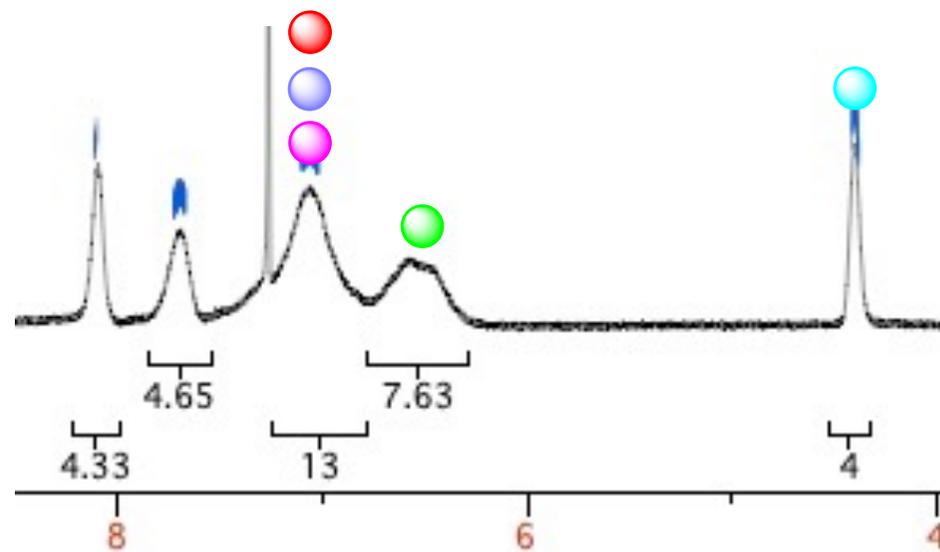
Entry	Styrene [eq.]	Conv. [%]	スチレン含有率 [%]	M n	M w / M n
1	0	93	0	8600	10.0
2	0.5	94	27	7200	16.3
3	1	94	38	7000	4.8
4	2	94	Frac. A 5, Frac. B 61	Frac. A 19000, Frac. B 4400	Frac. A 3.0, Frac. B 2.1
5	5	95	Frac. A 7, Frac. B 76	Frac. A 12000, Frac. B 3900	Frac. A 4.9, Frac. B 1.7



Fraction A

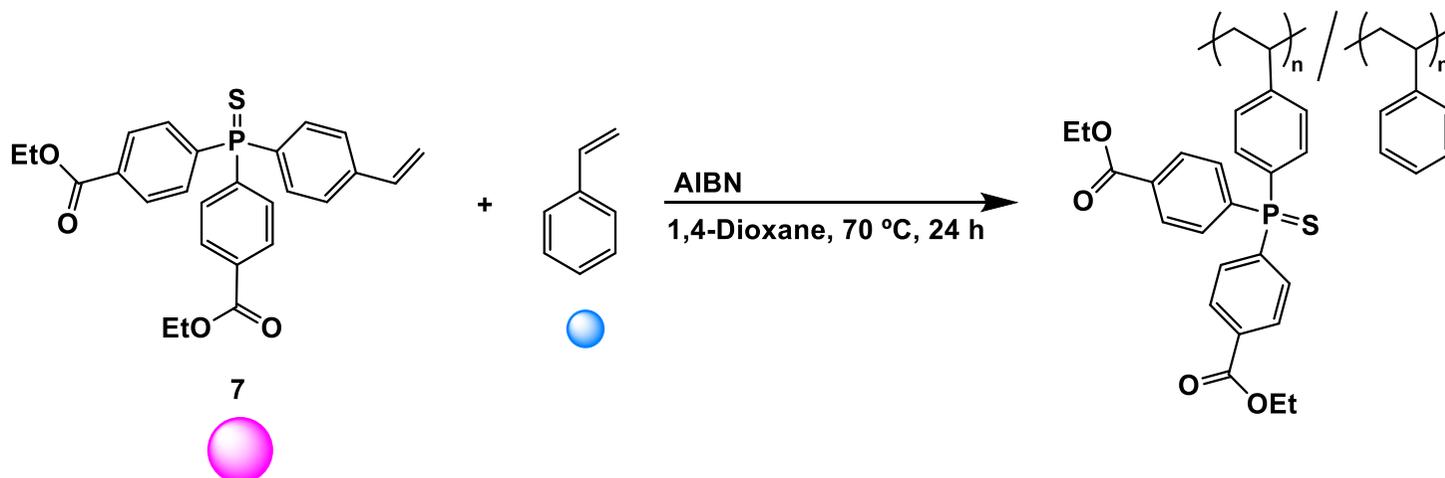


Fraction B



# 共重合体の推定モノマー配列

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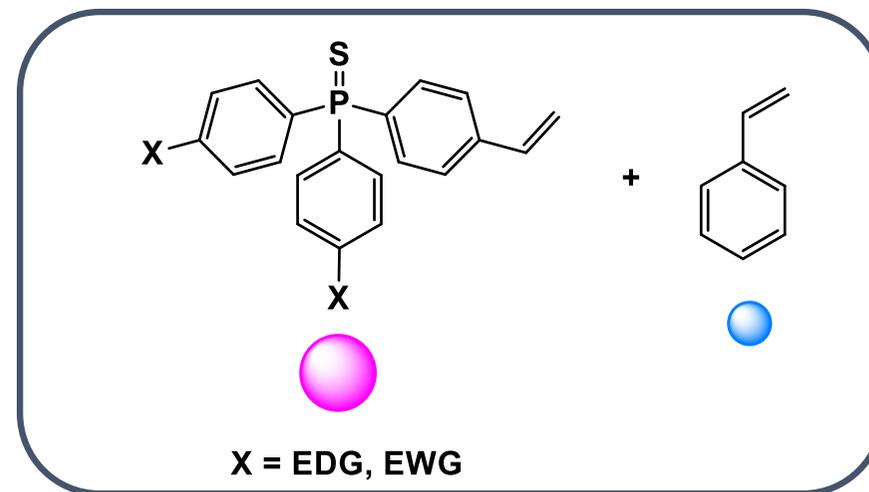
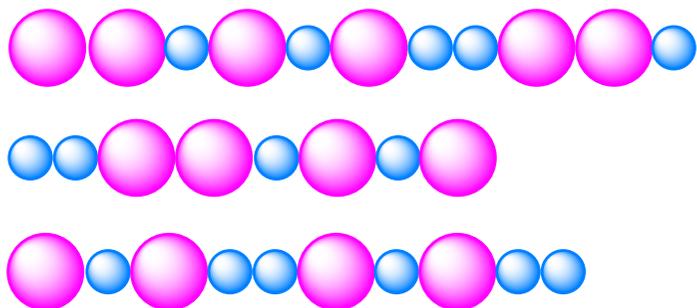
Fraction A (スチレン含有率 約7%)



Fraction B (スチレン含有率 76%)



電子供与基(  $-\text{C}_6\text{H}_4\text{OMe}$ ,  $-\text{C}_6\text{H}_4\text{Me}$  )



E. Okazaki, M. Hayashi, H. Ohta, *CSJ 105th Annual Meeting (2024)*, 2am-08

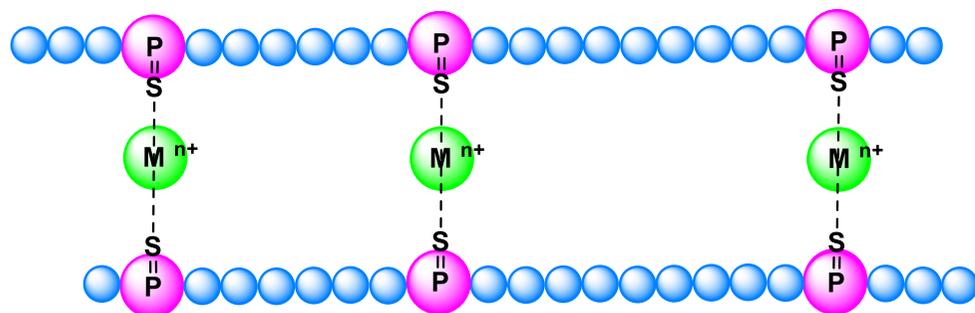
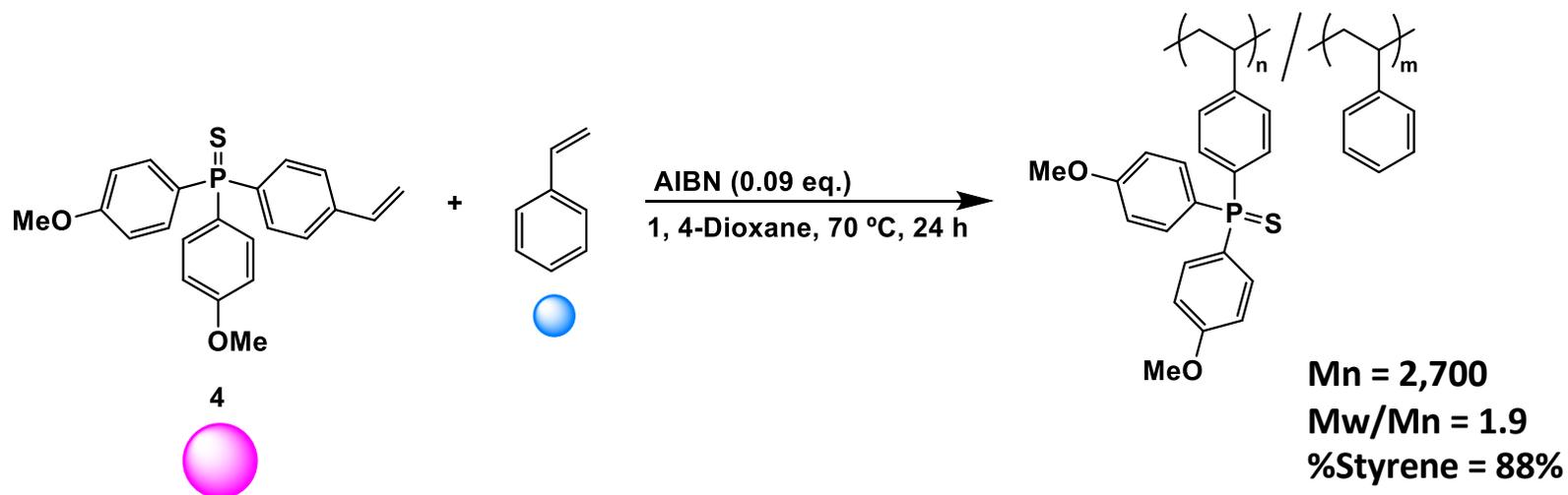
電子求引基(  $-\text{C}_6\text{H}_4\text{COOEt}$  )

Fraction A



Fraction B





$\text{Ti(OiPr)}_4 / \text{Toluene}$	×
$\text{TiCl}_4 / \text{Toluene}$	×
$\text{Zn(NO}_3)_3 \cdot 6\text{H}_2\text{O} / \text{THF, EtOH}$	×
$\text{ZnCl}_2 / \text{THF, EtOH}$	×

- ・ エステル基、メトキシ基を有するホスフィンスルフィドモノマーの合成に成功した
- ・ スチレンとの共重合挙動を明らかにした
- ・ モノマーとスチレンとの共重合体、モノマーの単独重合体の合成に成功した