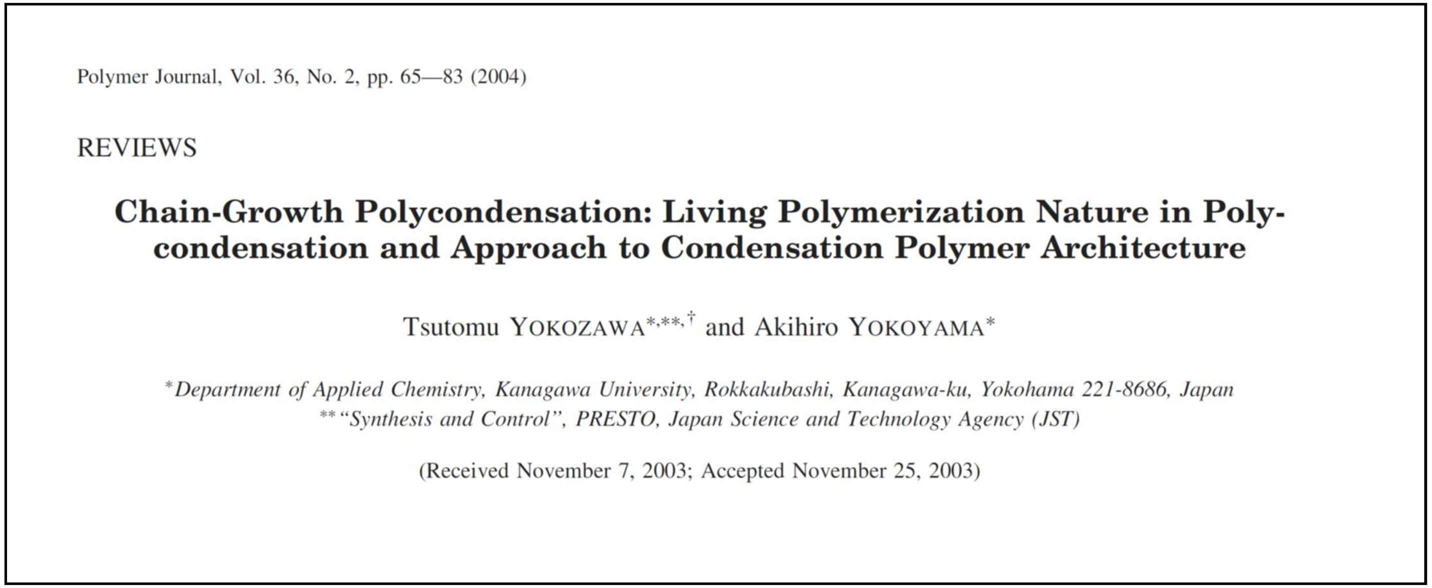
Living Step Polymerization



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REVIEWS

Chain-Growth Polycondensation: Living Polymerization Nature in Polycondensation and Approach to Condensation Polymer Architecture

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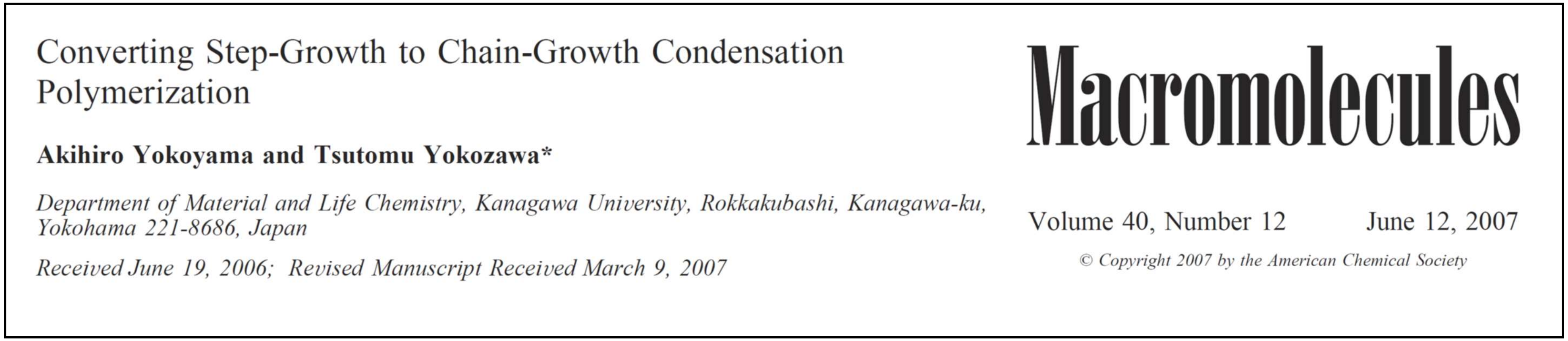

Converting Step-Growth to Chain-Growth Condensation Polymerization

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Questions

- What is one of the principal mechanistic reasons that prevents the synthesis of narrow dispersity polymers via conventional step polymerization chemistries ?
- Is it appropriate to draw parallels between living step polymerization, and the way in which proteins and DNA are synthesized in nature ?
- What other synthetic possibilites does living step polymerization provide access to, in addition to the ability to prepare narrow dispersity polymers ?

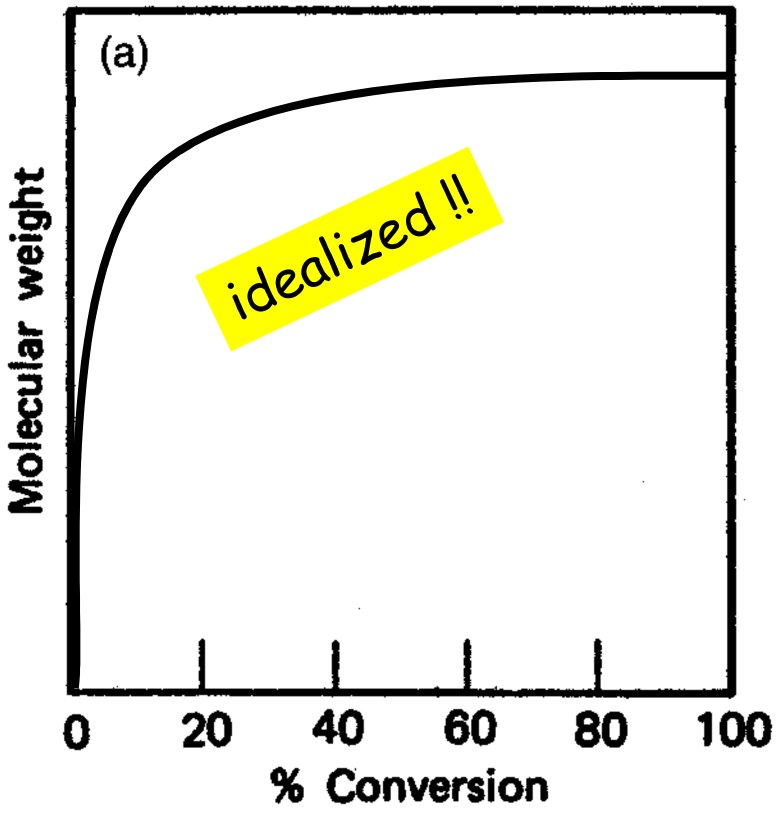
Step Polymerization

monomer + monomer → dimer
dimer + monomer → trimer
dimer + dimer → tetramer
trimer + monomer → tetramer
trimer + dimer → pentamer
trimer + trimer → hexamer
tetramer + monomer → pentamer
tetramer + dimer → hexamer
tetramer + trimer → heptamer
tetramer + tetramer → octamer
etc.

- Reaction occurs between any of the different sized species present in the reaction system
- Molecular weight increases relatively slowly with conversion

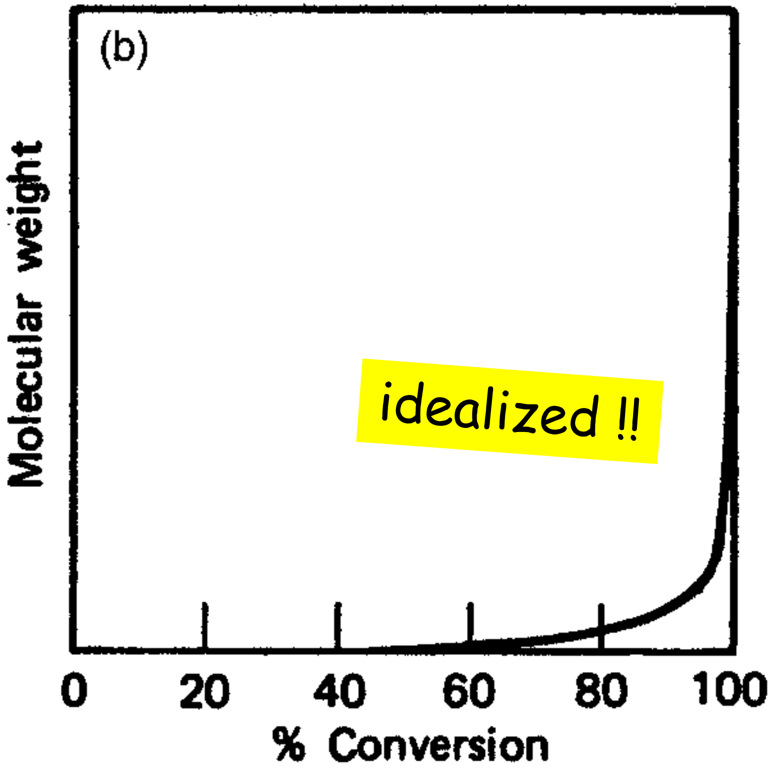
Schematic Development of Molecular Weight

chain polymerization



idealized !!

step polymerization



idealized !!

Some Definitions

- **Conversion (p)** The conversion is defined as: $p = \dfrac{[M]_0 - [M]}{[M]_0}$

[M] , $[M]_0$: concentration of reacting groups, i.e. the concentration of OH or COOH groups during polyester synthesis

- **Number-average degree of polymerization ($\overline{X}_n$, $\overline{P}$, $\overline{DP}$)**

1. The AB case: $$n\ \mathrm{HO\text{-}R\text{-}COOH} \rightarrow -[\overbrace{\mathrm{-O\text{-}R\text{-}(C{=}O)\text{-}}}^{\text{repeating unit}}]_n-$$

2. The AA + BB case: $$n\ \mathrm{HO\text{-}R'\text{-}OH} + n\ \mathrm{HOOC\text{-}R''\text{-}COOH} \rightarrow -[\overbrace{\underbrace{\mathrm{-O\text{-}R'\text{-}O\text{-}}}_{\text{structural/ monomer unit}}\underbrace{\mathrm{(O{=}C)\text{-}R''\text{-}(C{=}O)\text{-}}}_{\text{structural/ monomer unit}}}^{\text{repeating unit}}]_n-$$

$\overline{X}_n$, $\overline{P}$, $\overline{DP}$ =
Total number of molecules initially present/total number of molecules present at time t = Average number of repeat units per chain (AB polymerization) or the average number of structural units per chain (AA + BB polymerization):

$$\left.\begin{aligned} \overline{X}_n &= \frac{N_0}{N} = \frac{[\mathrm{M}]_0}{[\mathrm{M}]} \\ [\mathrm{M}] &= [\mathrm{M}]_0 - [\mathrm{M}]_0 p = [\mathrm{M}]_0(1-p) \end{aligned}\right\} \quad \overline{X}_n = \frac{1}{(1-p)}$$

Carothers equation

Assumption: equimolar quantities of reacting groups A and B

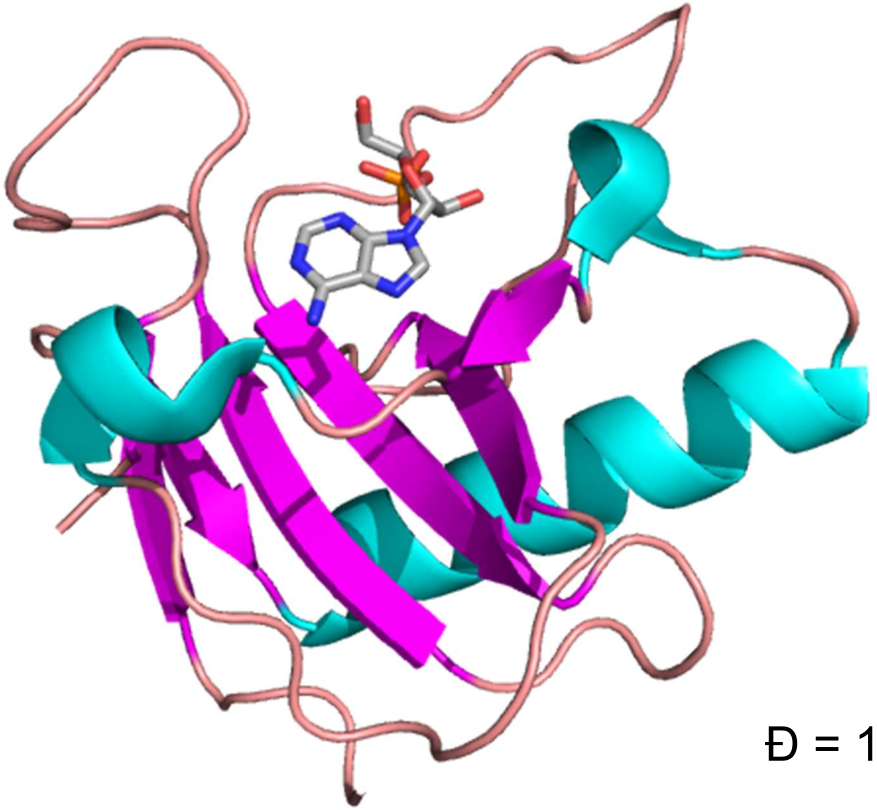
Breadth of the Molecular Weight Distribution

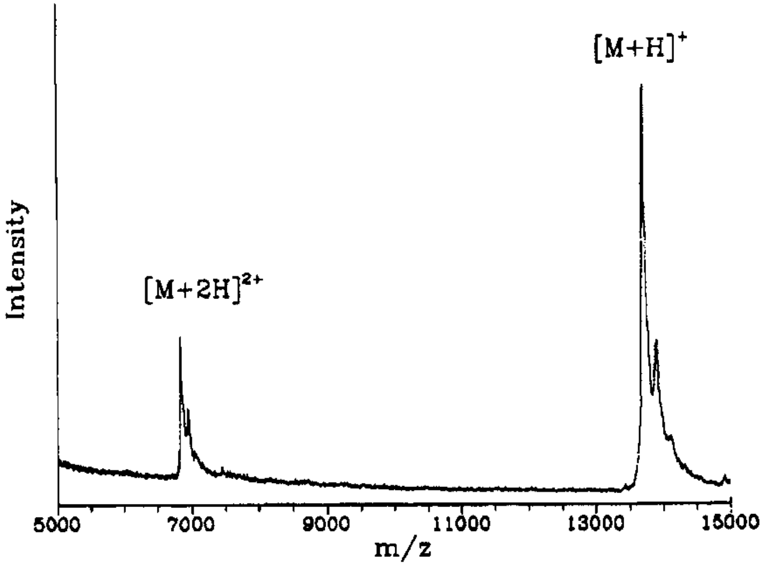
$$\overline{X}_n = \frac{1}{(1-p)} \qquad \overline{X}_w = \frac{(1+p)}{(1-p)} \qquad \frac{\overline{X}_w}{\overline{X}_n} = (1+p)$$

X_w/X_n synonymous with M_w/M_n = polydispersity index (PDI)

The Quest for One

Proteins: Perfect control of chain length and sequence





(Anal. Chem. **1990**, 62, 1836)

Đ = 1.0

Ribonuclease A: molecular weight = 13 690,29 gr/mol
124 amino acids (degree of polymerization = 124)

Characteristics of Living Polymerizations(*)

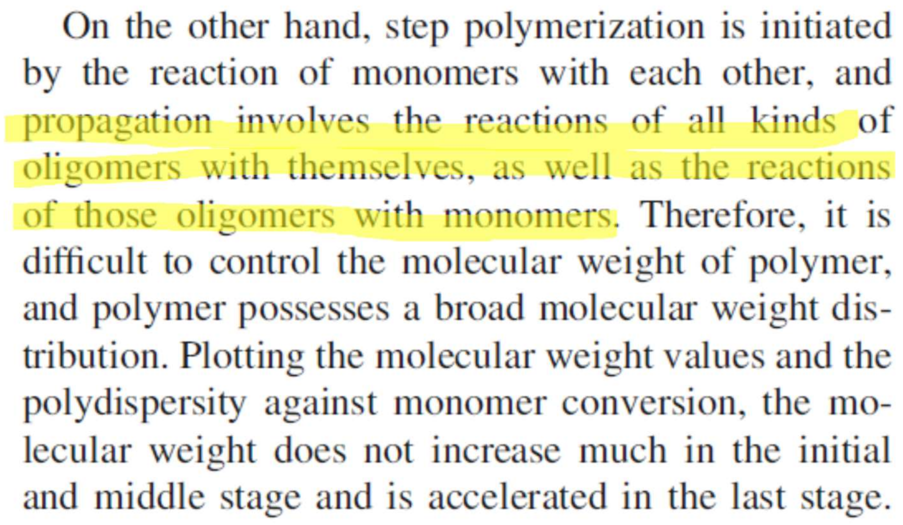
Linear evolution of MW with conversion.
$MW < \Delta[M]/[I]_0$ = transfer;
$MW > \Delta\ [M/[I]_0$ inefficient initiation or
chain coupling

Dispersity (Đ; M_w/M_n) close to Poisson distribution ($M_w/M_n \approx 1 + 1/DP_n$)

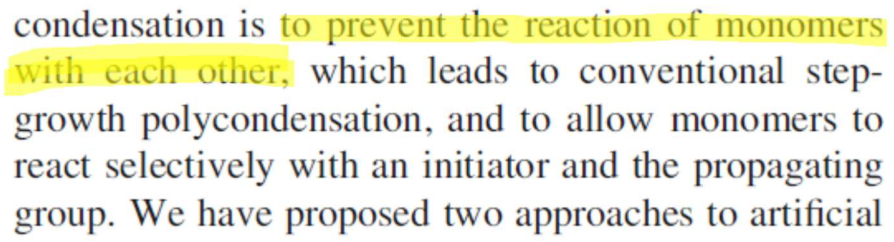
End-functionality is not affected by slow initiation and exchange but is reduced when chain breaking reactions become important

(*) see also radical chain, and controlled radical polymerization / ionic chain polymerization

The Problem, and The Way Out



On the other hand, step polymerization is initiated by the reaction of monomers with each other, and propagation involves the reactions of all kinds of oligomers with themselves, as well as the reactions of those oligomers with monomers. Therefore, it is difficult to control the molecular weight of polymer, and polymer possesses a broad molecular weight distribution. Plotting the molecular weight values and the polydispersity against monomer conversion, the molecular weight does not increase much in the initial and middle stage and is accelerated in the last stage.



condensation is to prevent the reaction of monomers with each other, which leads to conventional step-growth polycondensation, and to allow monomers to react selectively with an initiator and the propagating group. We have proposed two approaches to artificial

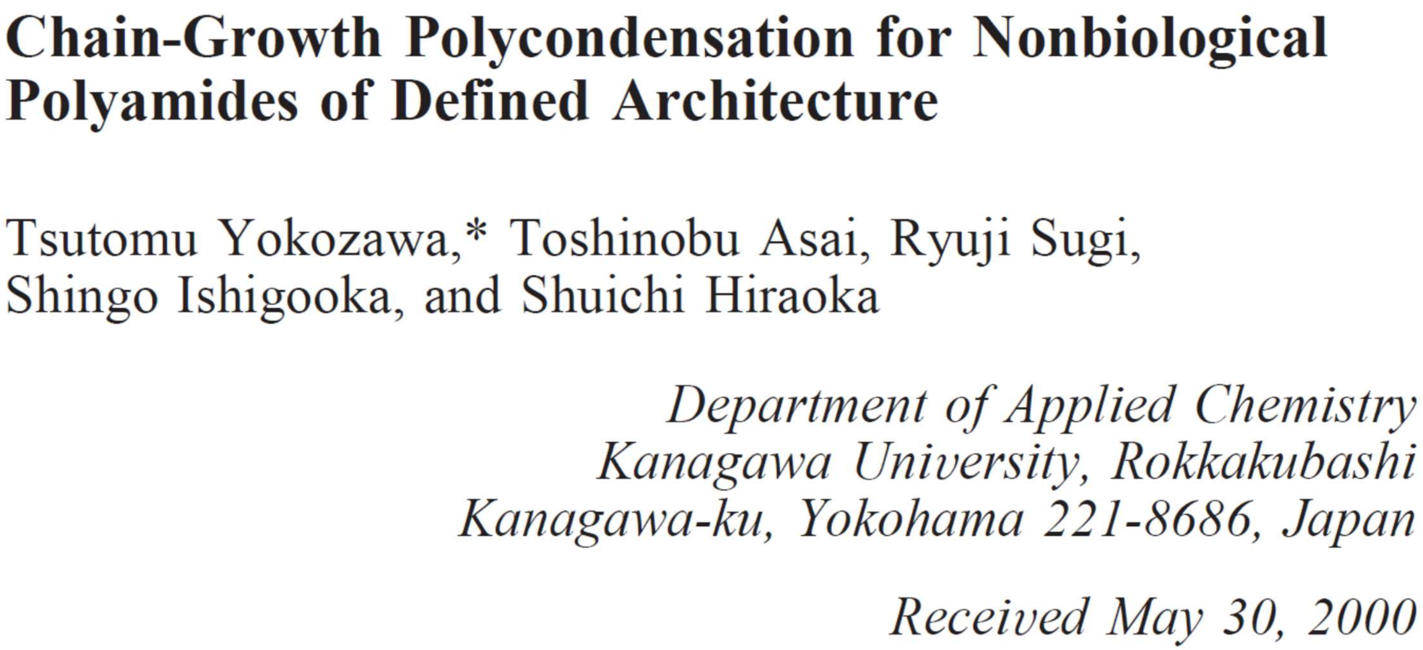
Polymer Journal **2004**, *36*, 65-83

Living Step Polymerization

1) Based on the substituent effect

2) By catalyst transfer

Based on the Substituent Effect



Chain-Growth Polycondensation for Nonbiological Polyamides of Defined Architecture

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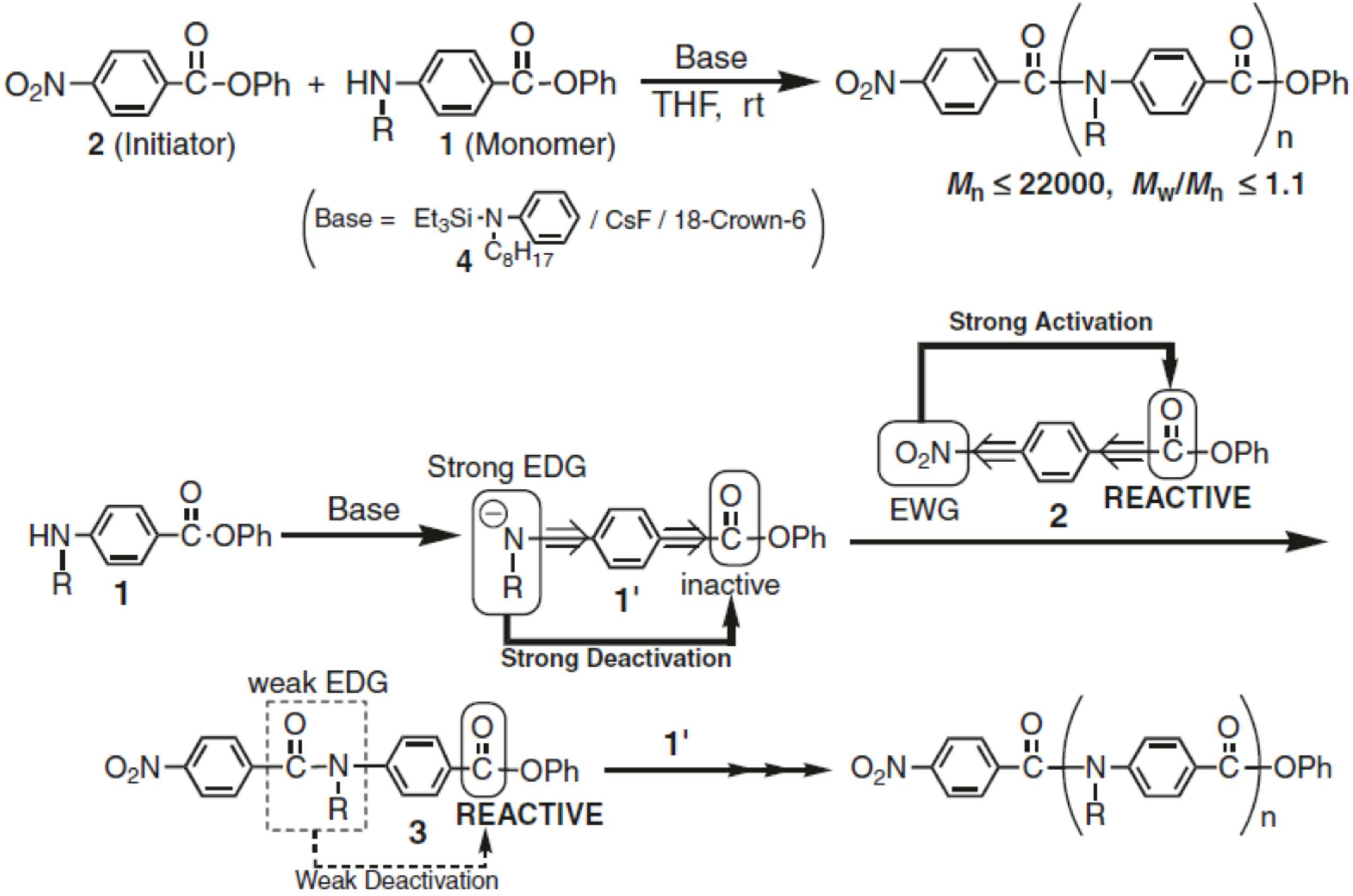

(EDG: Electron-donating group; EWG: Electron-withdrawing group)

Original reference: *J. Am. Chem. Soc.* **2000,** *122,* 8313-8314

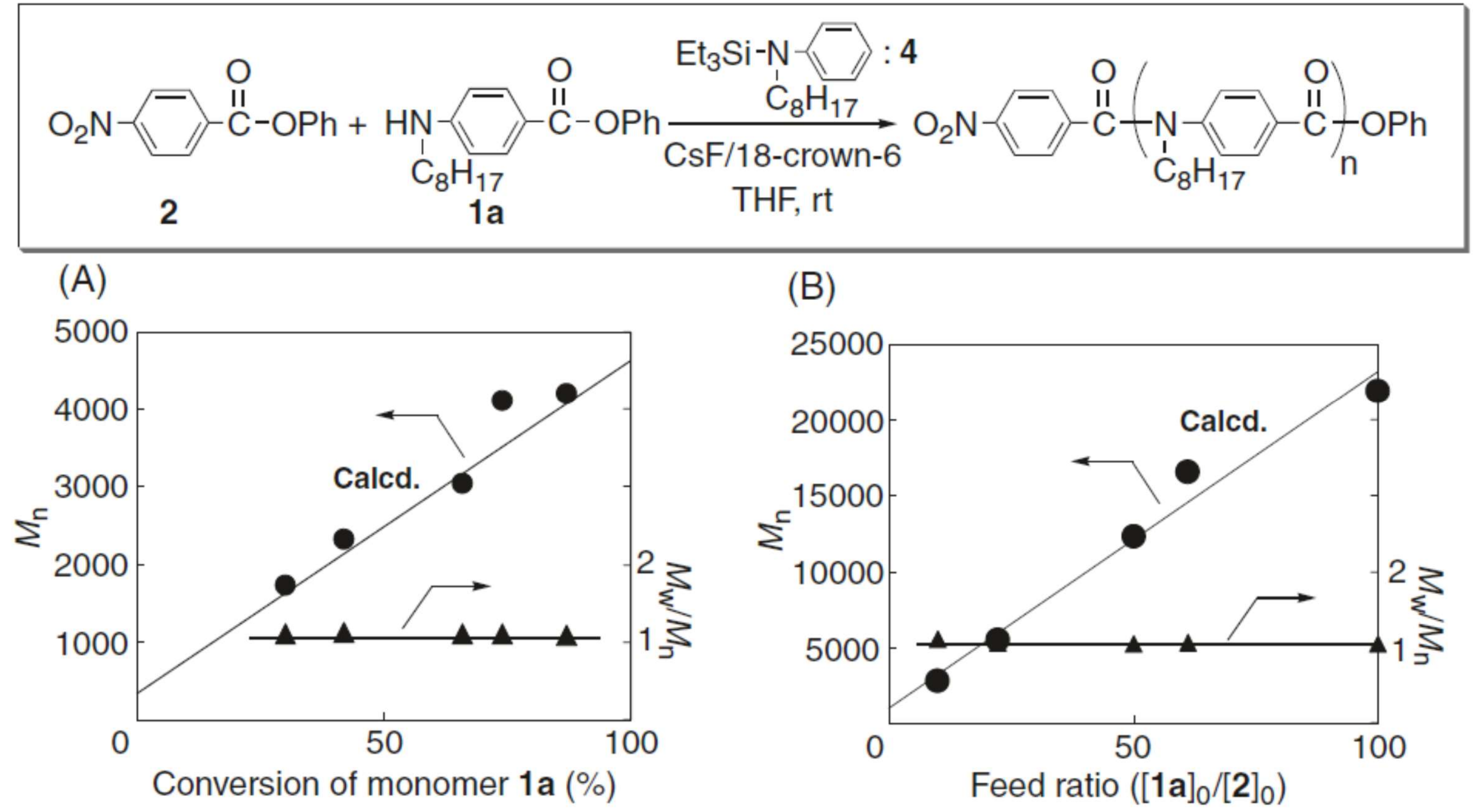

Figure 1. (A) M_n and M_w/M_n values of poly**1a**, obtained with **4**/CsF/18-crown-6 in the presence of **2** in THF at 25 °C, as a function of monomer conversion: $[\mathbf{1a}]_0 = 0.33$ M; $[\mathbf{4}]_0 = 0.31$ M; $[\text{CsF}]_0 = 0.33$ M; $[\text{18-crown-6}]_0 = 0.67$ M; $[\mathbf{2}]_0 = 0.018$ M. The line indicates the calculated M_n values assuming one polymer chain per unit **2**. (B) M_n and M_w/M_n values of poly**1a**, obtained with CsF/18-crown-6 in the presence of **2** in THF at 25 °C, as a function of the feed ratio of **1a** to **2**: $[\mathbf{1a}]_0 = 0.67$ M; $[\mathbf{4}]_0 = 0.73$ M; $[\text{CsF}]_0 = 0.67$ M; $[\text{18-crown-6}]_0 = 1.3$ M; $[\mathbf{2}]_0 = 6.7$–67 mM; conversion = 100 %. The line indicates the calculated M_n values assuming one polymer chain per unit **2**.

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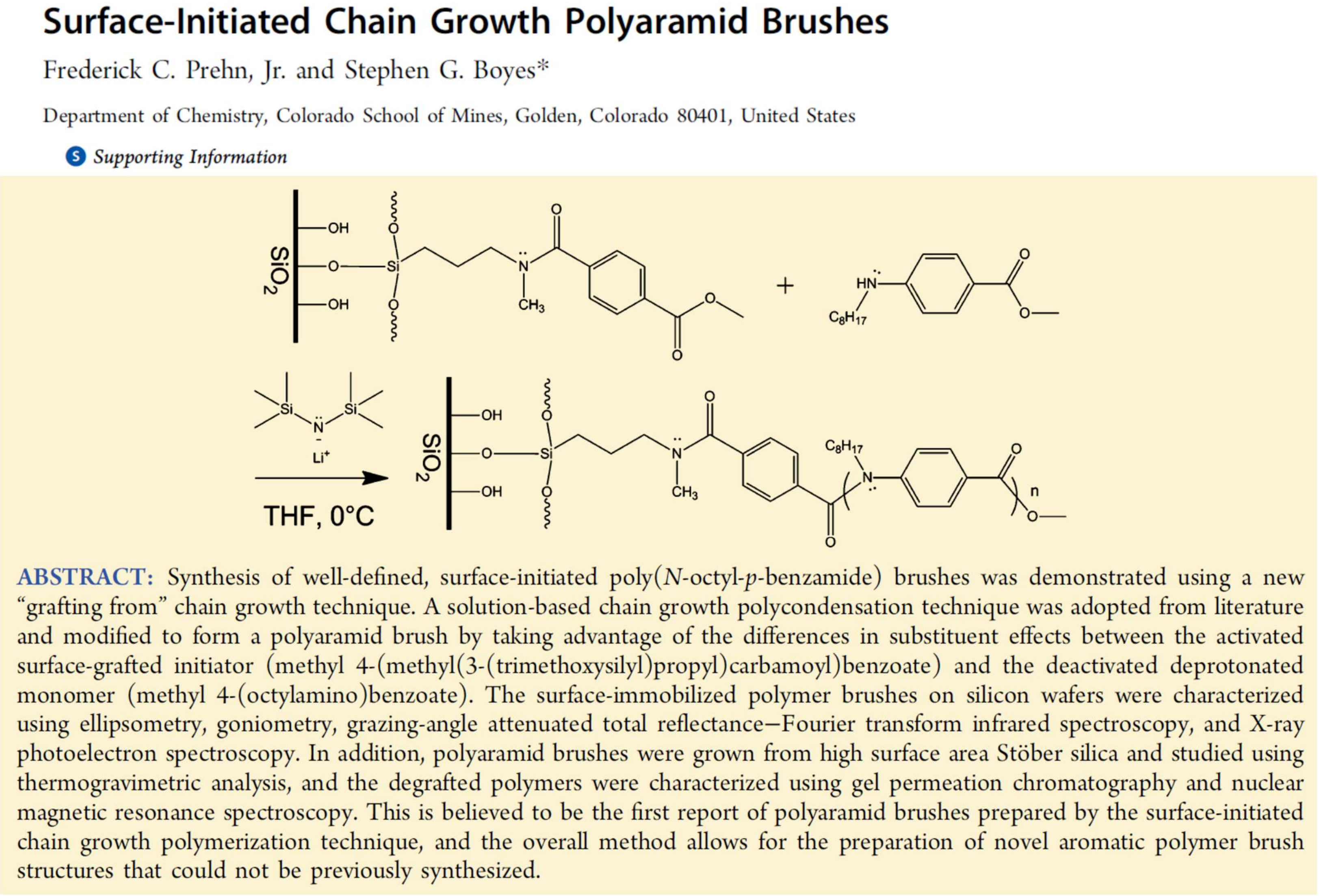
Polymerization from Surfaces



Surface-Initiated Chain Growth Polyaramid Brushes

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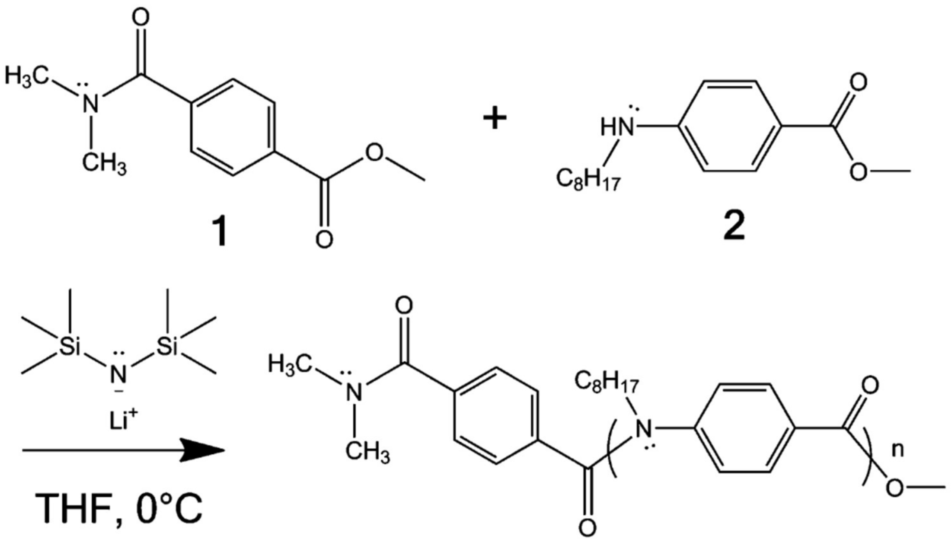
Supporting Information

ABSTRACT: Synthesis of well-defined, surface-initiated poly(*N*-octyl-*p*-benzamide) brushes was demonstrated using a new "grafting from" chain growth technique. A solution-based chain growth polycondensation technique was adopted from literature and modified to form a polyaramid brush by taking advantage of the differences in substituent effects between the activated surface-grafted initiator (methyl 4-(methyl(3-(trimethoxysilyl)propyl)carbamoyl)benzoate) and the deactivated deprotonated monomer (methyl 4-(octylamino)benzoate). The surface-immobilized polymer brushes on silicon wafers were characterized using ellipsometry, goniometry, grazing-angle attenuated total reflectance–Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy. In addition, polyaramid brushes were grown from high surface area Stöber silica and studied using thermogravimetric analysis, and the degrafted polymers were characterized using gel permeation chromatography and nuclear magnetic resonance spectroscopy. This is believed to be the first report of polyaramid brushes prepared by the surface-initiated chain growth polymerization technique, and the overall method allows for the preparation of novel aromatic polymer brush structures that could not be previously synthesized.

Macromolecules **2015**, *48*, 4269−4280.

Model, solution polymerization experiments



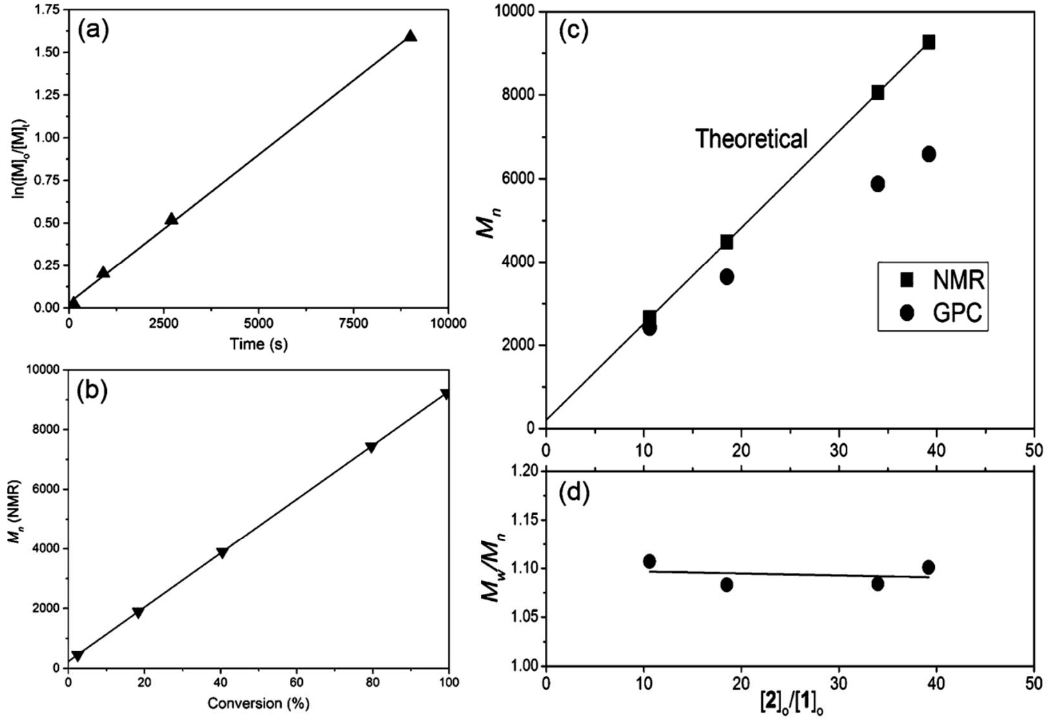
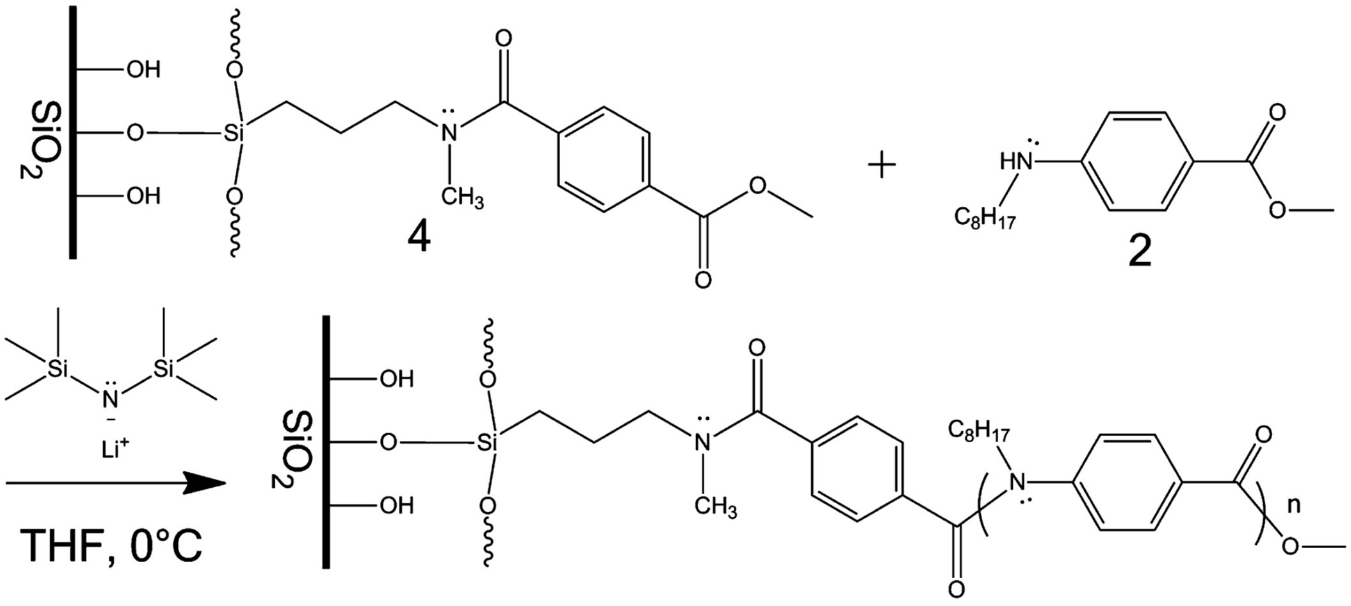
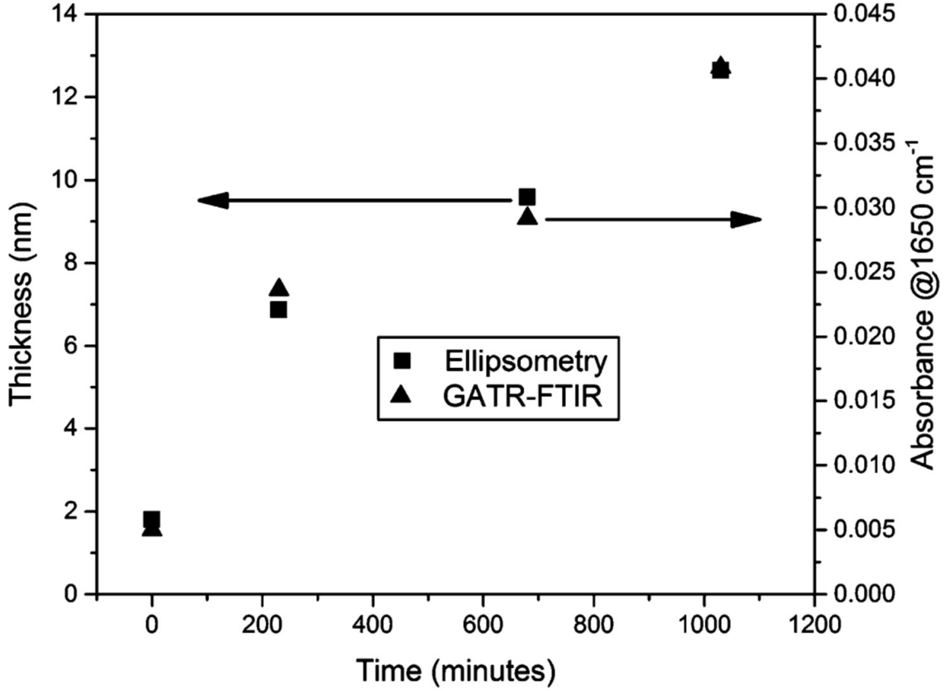


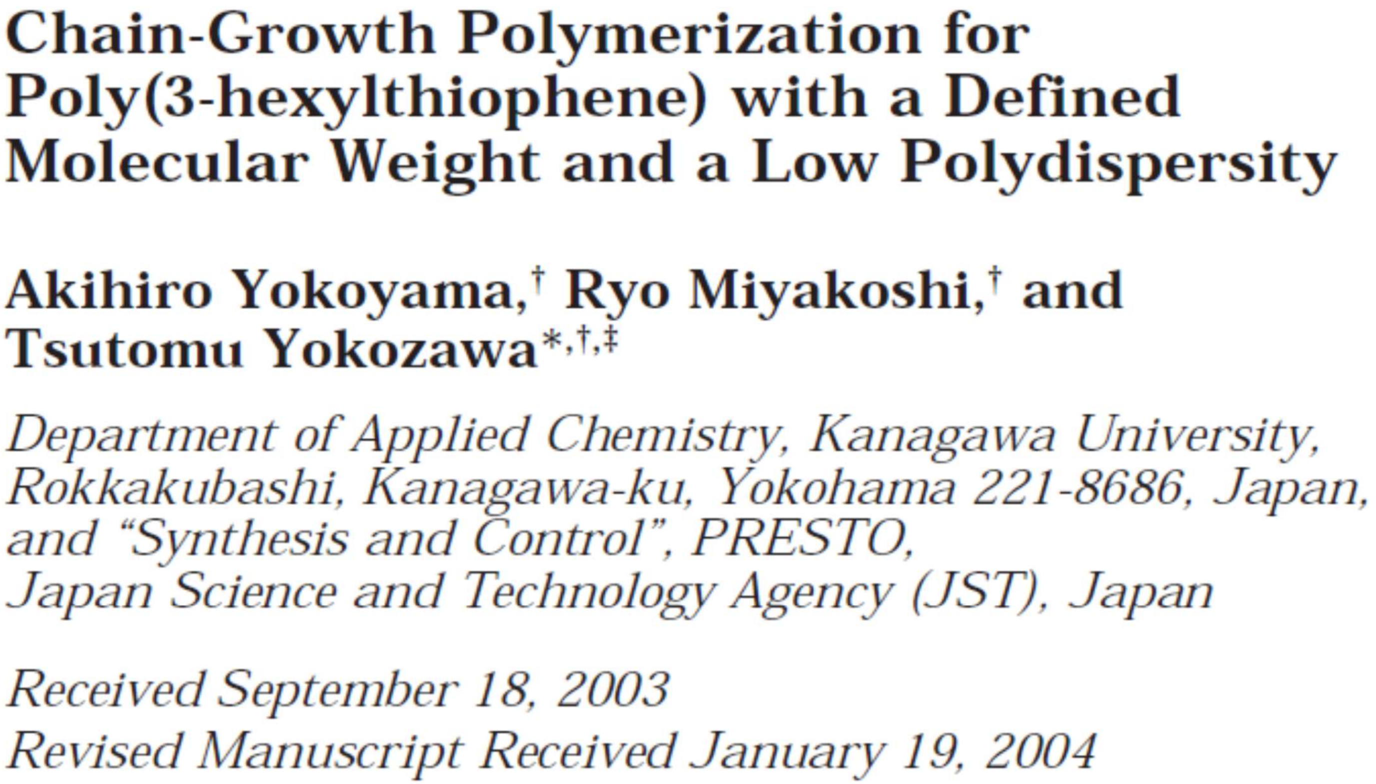
Figure 1. (a) Semilogrithmic plot, (b) the correlation between M_n and conversion from kinetics samples, (c) calculated M_n values resulting from initial feed ratio of **2**:**1** after 100% conversion calculated from NMR and GPC, and (d) M_w/M_n calculated from GPC of samples in (c) all demonstrating the well-controlled CGC polymerization.





Polymerization from surfaces

By Catalyst Transfer



Chain-Growth Polymerization for Poly(3-hexylthiophene) with a Defined Molecular Weight and a Low Polydispersity

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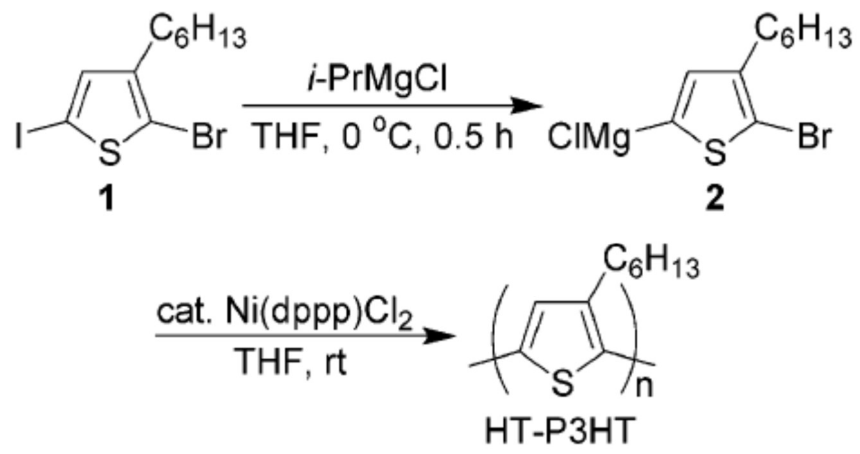
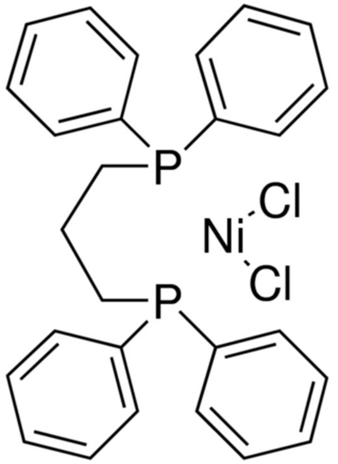


(**1**): 2-bromo-3-hexyl-5-iodothiophene



Ni(dppp)Cl_2

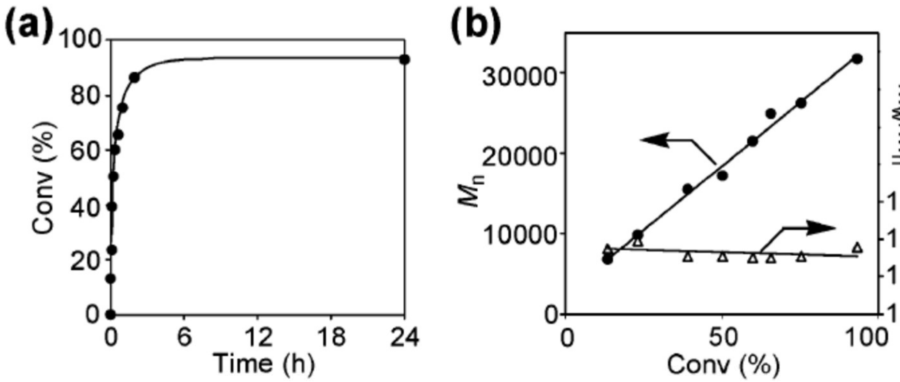


Figure 1. Polymerization of **2** with 0.4 mol % of Ni(dppp)Cl_2 in THF at room temperature ($[\mathbf{2}]_0$ = 0.12 M): (a) time–conversion curve; (b) M_n and M_w/M_n values of HT-P3HT as a function of monomer conversion.

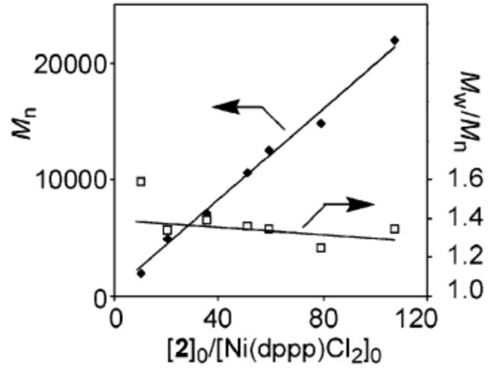
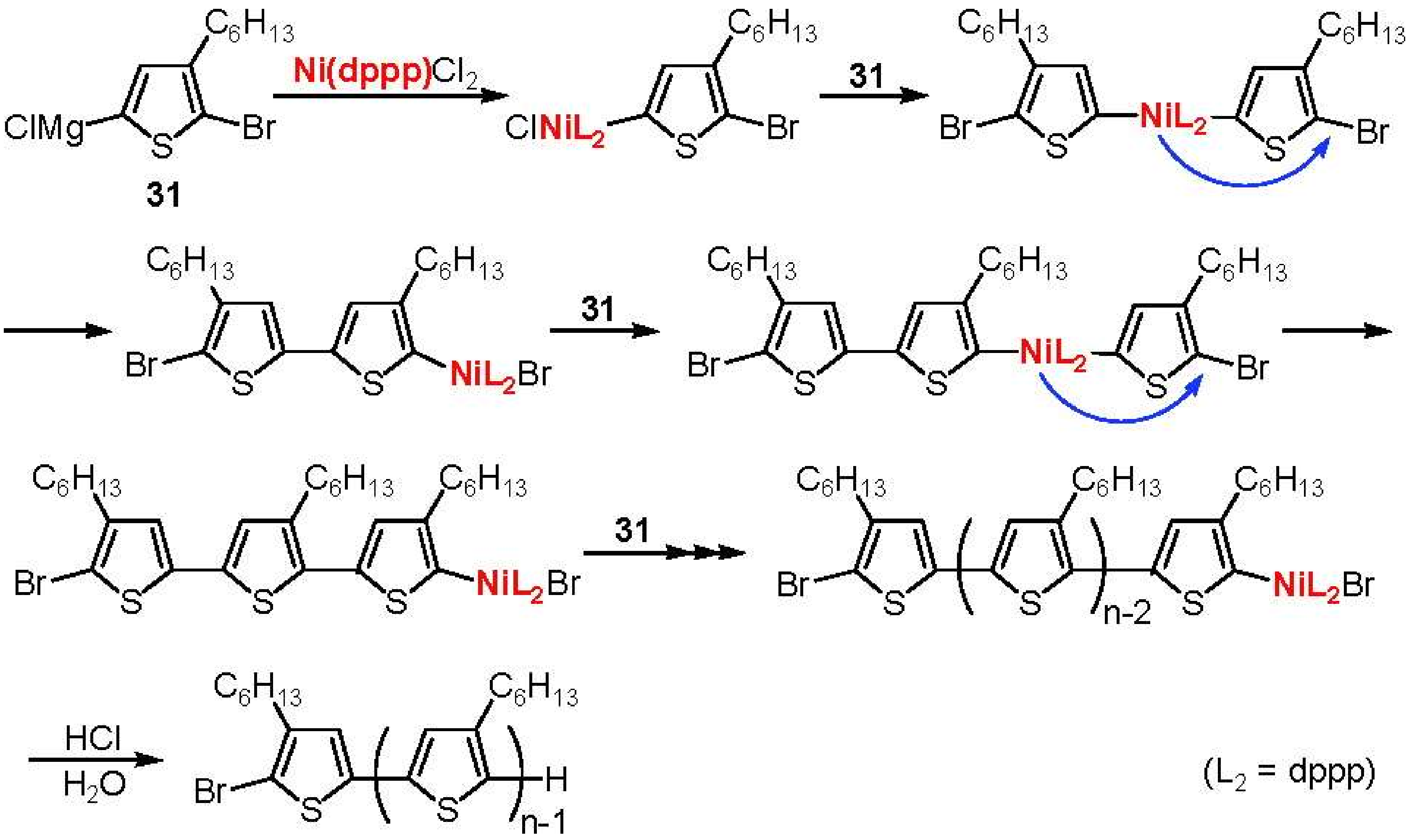


Figure 2. M_n and M_w/M_n values of HT-P3HT, obtained with **2** and Ni(dppp)Cl_2 in THF at room temperature, as a function of the feed ratio of **2** to Ni(dppp)Cl_2: $[\mathbf{2}]_0$ = 0.12 M; $[\text{Ni(dppp)Cl}_2]_0$ = 1.1−11.8 mM; conversion = 86−93%.

Original reference: *Macromolecules* **2004,** *37,* 1169-1171



“Thus, the polymerization is initiated by the reaction of the Ni catalyst with two molecules of the monomer ***31****. After formation of the bithiophene by reductive elimination, the Ni catalyst transfers intramolecularly to the terminal C-Br bond. Propagation would proceed through reaction of* ***31*** *with the Ni complex at the polymer growing end, followed by intramolecular transfer of the Ni catalyst. In this way, the monomer reacts selectively at the polymer propagating end to result in chaingrowth polymerization. We call this type of polymerization catalyst-transfer condensation polymerization.”*

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Learning Objectives

- Understand the mechanistic reasons that prevent the synthesis of narrow dispersity polymers via conventional step polymerization chemistries.
- Describe, conceptually, what it takes to tranform a conventional step polymerization into a living polymerization process.
- Be familiar with two main principal approaches that exist to perform living step polymerization reactions.