Living polymerization

Polymers in everday use

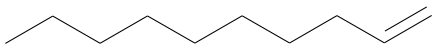
- Mechanical properties
- New applications
- Personal care products
- Pharmaceutical Applications
- BASF, Unilever, Geltex, Avecia, etc

Control over Polymer architecture

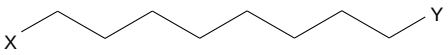
- Graft Copolymers
- Star copolymers
- Dendrimers
- Non covalent crosslinking
- Branching
- Narrow MWD
- Blocks

Control

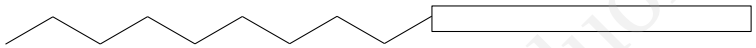
Macromonomer



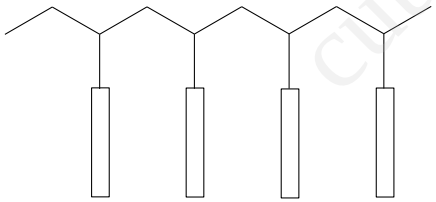
Telechelic



Block

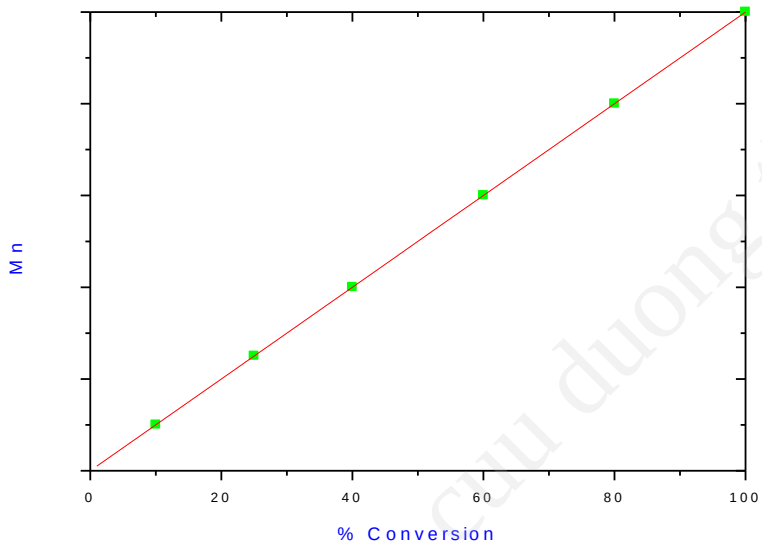


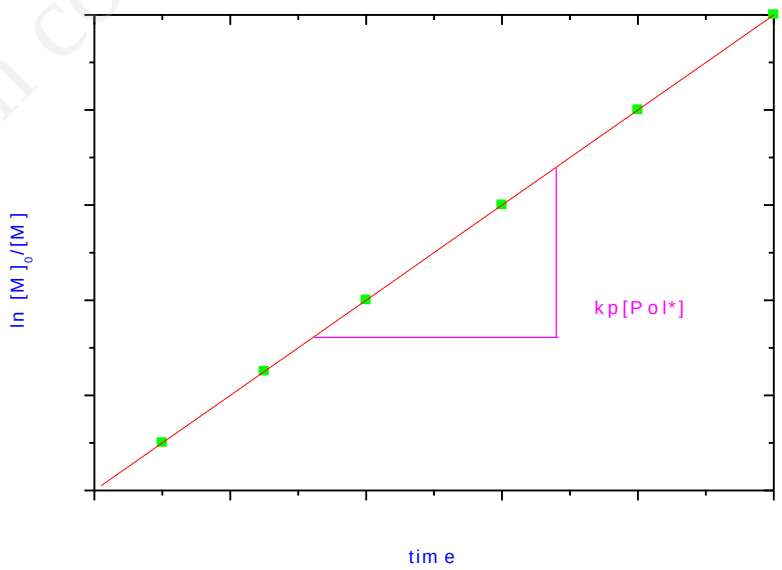
Graft



- Molecular Weight
  (Chain Length and Polydispersity)
- Chain Architecture
  (Block, Comb, etc)
- Functionality
- Rate / Exotherm

Test for Living Polymerisation





Living Polymerisation

- Anionic
- Cationic
- Ring Opening

Living Polymerisation

- Rate of termination ~ 0
- Rate of Initiation > Rate of Propagation
- PDi (Mw/Mn) = 1 + 1/DP

Living systems

*constant number of polymer chains

*no permanent chain stopping reactions

*dormant and active state

*control of chain-growth

*narrow MWD (Poisson)

*<*Mn*> vs. monomer conversion is linear

Living Polymerisation

- No Termination
- No Chain Transfer

INITIATION

$$I^* + M \rightarrow IM^* \qquad k_i$$

PROPAGATION

$$IM^* + M \rightarrow IMM^* \qquad k_{p1}$$

$$IM_n^* + M \rightarrow IM_nM^* \qquad k_{pn}$$

Rate of Initiation $= k_i[I][M]$

Rate of Propagation $= k_p[M^*][M]$

$$[M^*] = [I]$$

Integration leads to,

$$\ln[M]_0/[M] = k_p[M^*]t$$

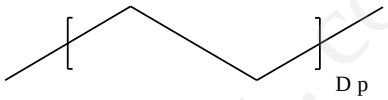
As the rate of termination = 0

$[M^*]$ is constant

Thus a plot of $\ln[M]_0/[M]$ vs t is linear

Degree of Polymerisation = Dp_n

i.e.



$Dp_n = [M]/[I]$ @ 100% conversion

$Mn = Dp_n \times M_0$

(M_0 = mass of the repeat unit)

Thus a plot of Mn vs % Conversion is linear for a living polymerisation

If Rate of initiation (R_i) $\approx$ or > Rate of Propagation (R_p)

and both R_i and R_p > Rate of termination (R_t)

(Ideally $R_t = 0$)

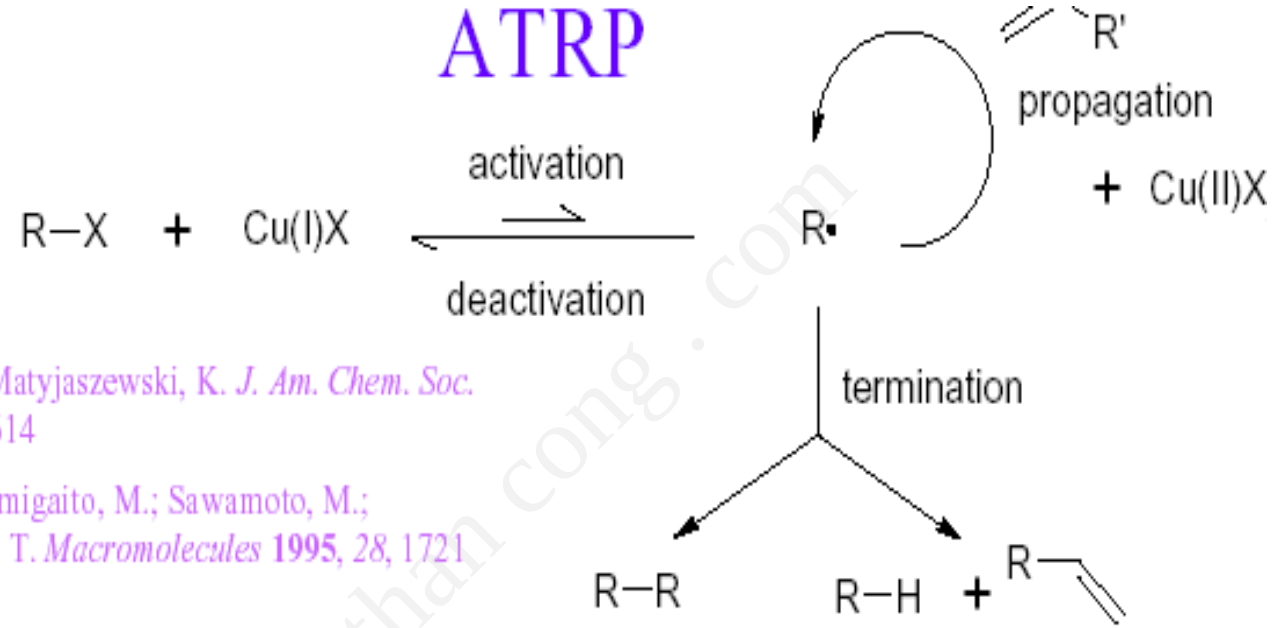
Then

PDi (MWD, Mn/Mw) is narrow and a Poisson distribution.

$$PDi = 1 + 1/[DP_n]$$

e.g. For a polymer with DPn = 100, PDi = 1.01

ATRP

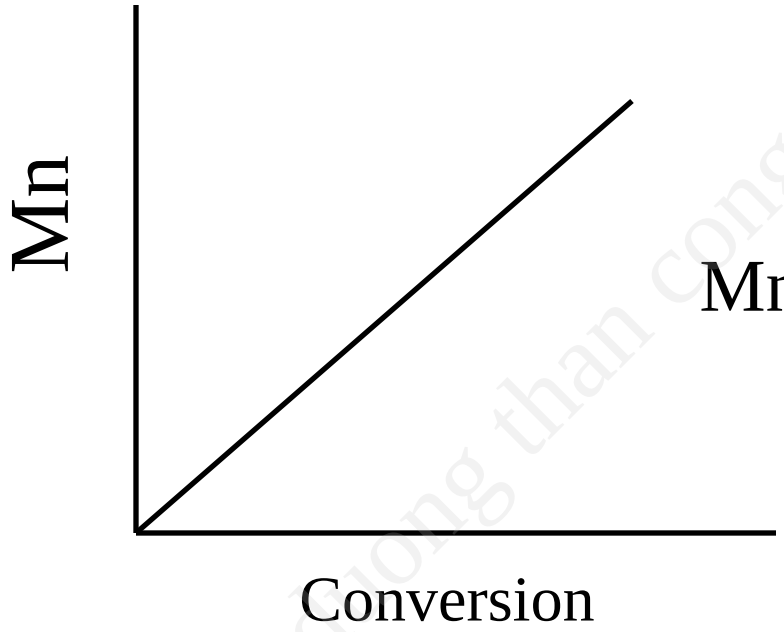


Wang, J-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614

Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721

- Usually copper, but other metals can be used.
- Usually in organic solvent at elevated temperatures.
  - Low M_w/M_n (~1.1-1.2) possible.
  - Synthesis of block copolymers possible by macro-initiator route or by sequential monomer addition (in some cases).

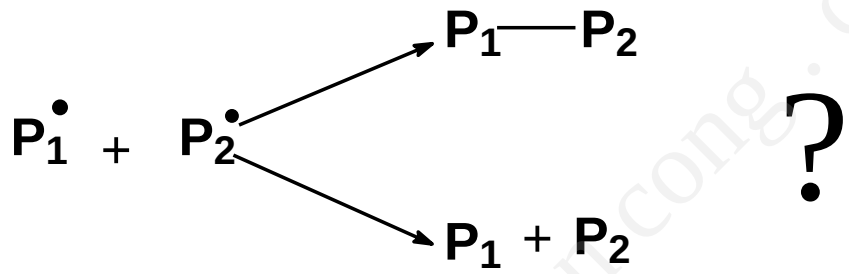
Living Polymerization

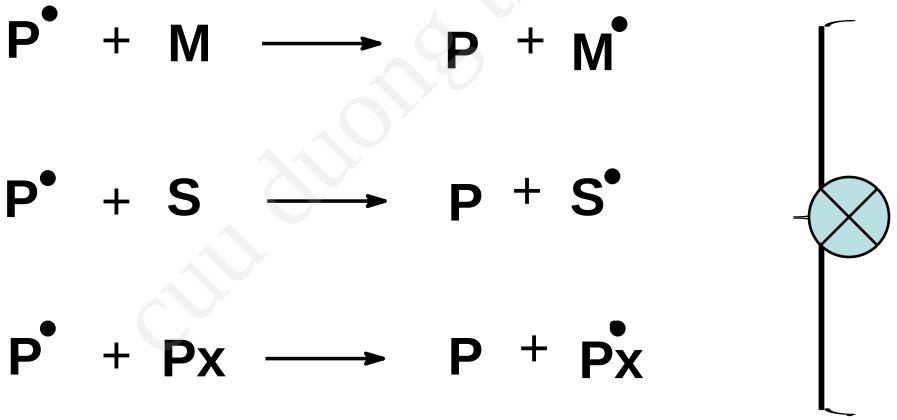


$$Mn = \frac{[M]_0}{[I]_0} \times M_m \times Conv.$$

- Mn
- Structure

Radical reactions





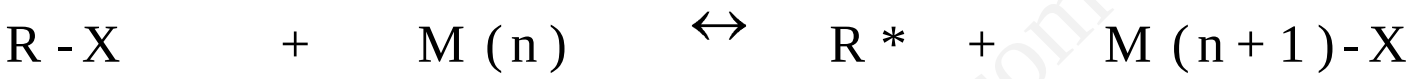
Free Radical Polymerisation

- Widely used industrially
- Advantages:
  - Very Robust Technique
  - Wide range of monomers and functionality's
    Almost anything with a double bond
  - Wide range of operating conditions
  - Aqueous Media: Emulsion polymerisation
- Disadvantages
  - Highly non-selective reaction

Non-trivial product control

Living and Controlled Polymerisations

- **Living systems**
  - constant number of polymer chains
  - no permanent chain stopping reactions
  - dormant and active state
  - control of chain-growth
  - narrow MWD (Poisson)
  - $<M_n>$ vs. monomer conversion is linear



X = Cl, Br

R* can propagate or terminate

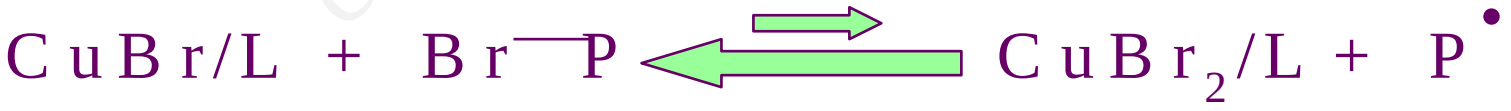
K. Matyjaszewski: Macromolecules **1997**, *30*, p7697; 7042; 7034; 7348; 8161; 7692; 6507, 6513, 6398 JACS **1997**, *119*, p674
V Percec: Macromolecules **1997**, *30*, p6705, 8526
M Sawamoto: Macromolecules **1997**, *30*, p2244, 2249
Teyssie: Macromolecules **1997**, *30*, p7631,
Haddleton: Macromolecules **1997**, *30*, p2190

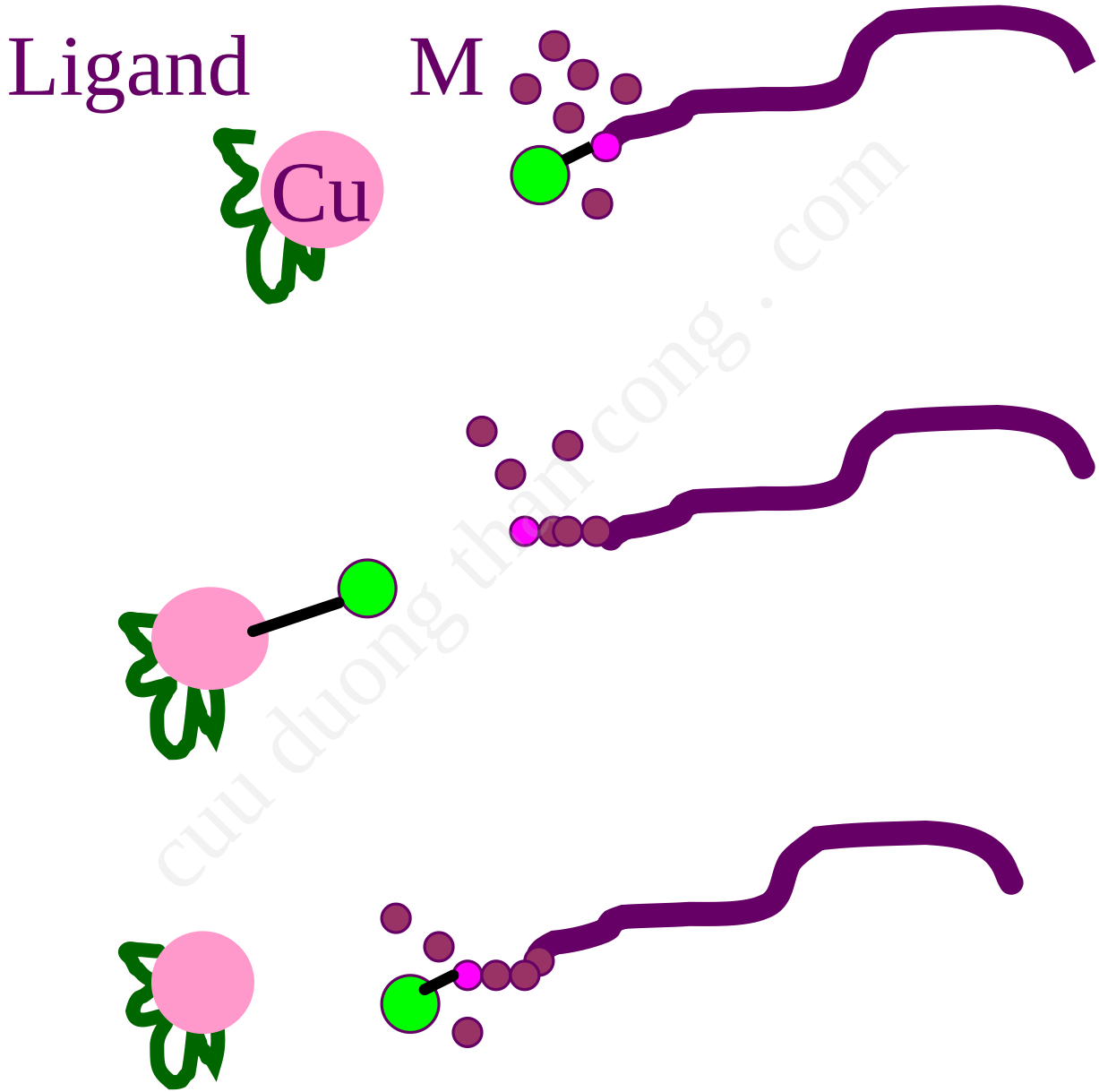
Suppressing radical termination

$$Rt/Rp = k_t [P^\bullet]^2 / k_p [M][P^\bullet]$$

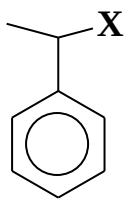
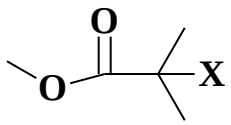
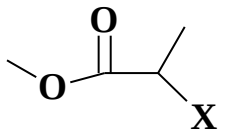
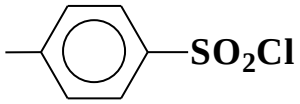
$$= k_t [P^\bullet] / k_p [M]$$

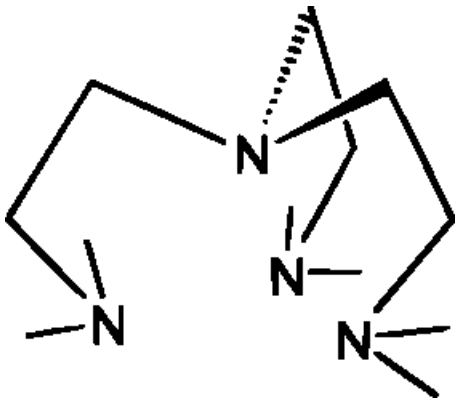
ATRP Mechanism

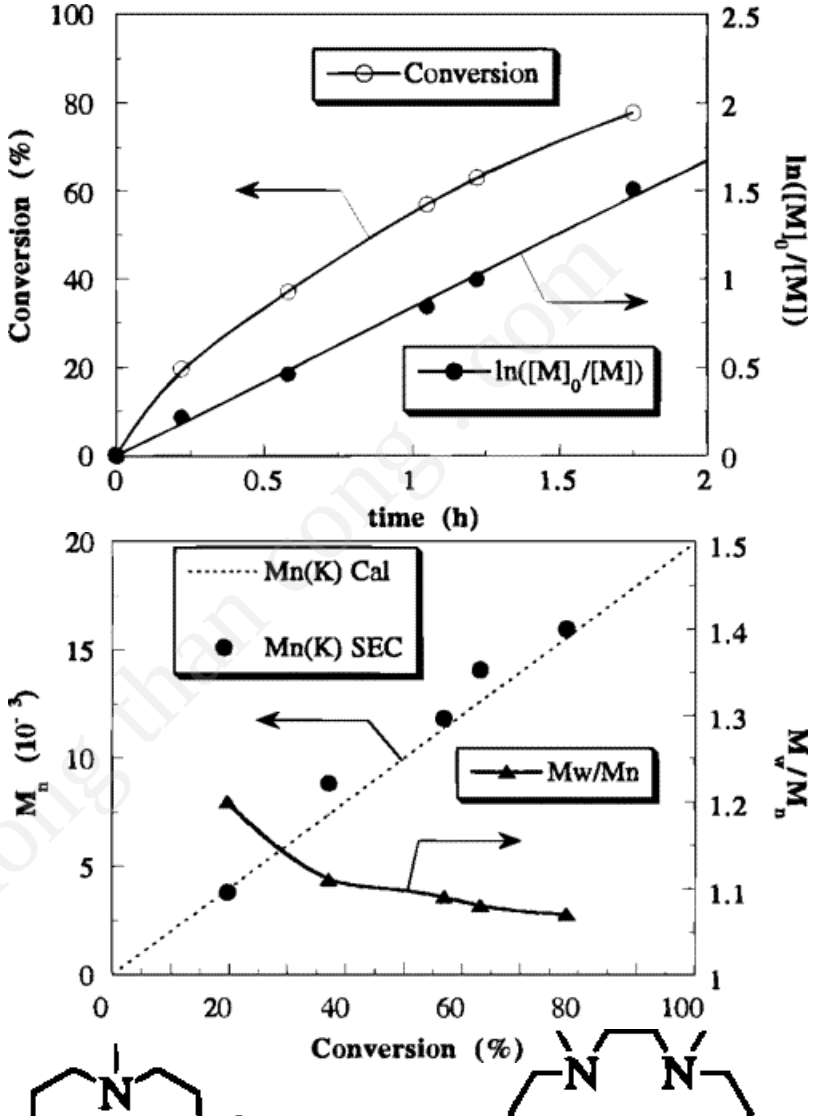


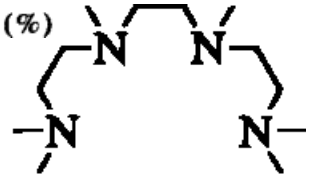


ATRP Systems

Metal	Ligand	Initiator
CuBr, CuCl	Bipyridine	
	Multidentate amine	
$RuBr_2$	$PPh_3 + Al(OiPr)_3$	
$FeBr_2$	PPh_3	
$NiBr_2$	PPh_3	
$PdBr_2$	PPh_3	
		





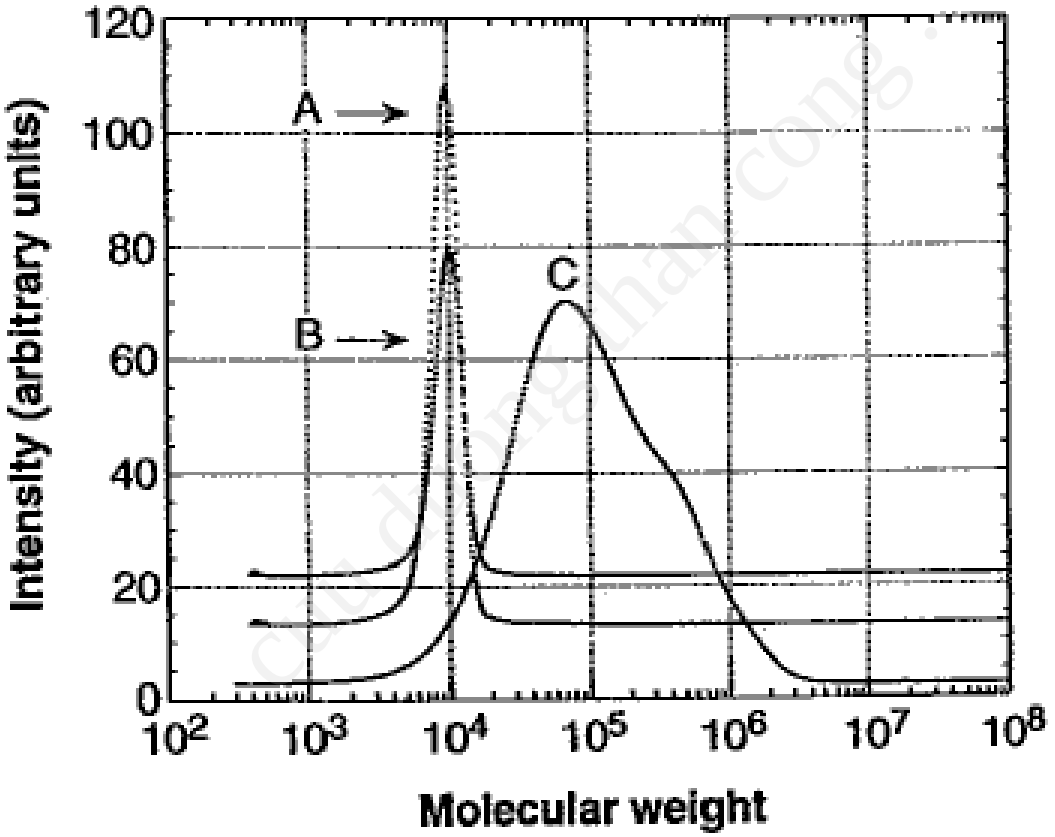


TMEDA **PMDETA** **HMTETA**

Macromolecules, 30 (25), 7697 -7700, 1997.

2. ATRP Applications

A: Synthesis of polymers with controlled molecular weight



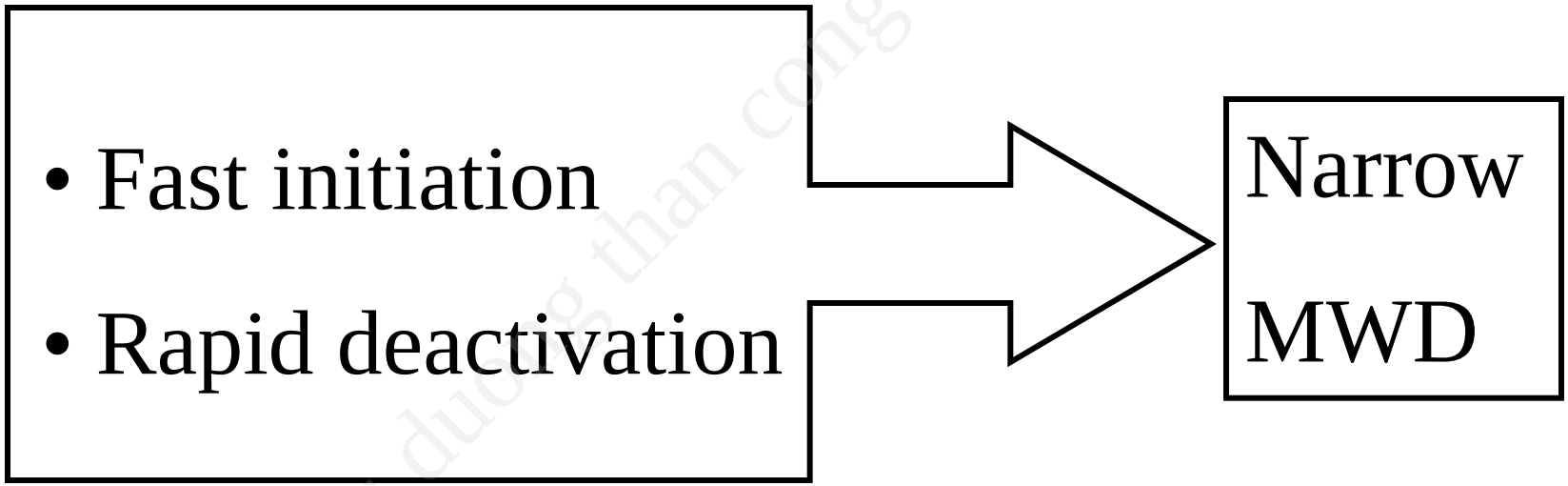
A: PS standard

B: PS by ATRP

C: PS by AIBN

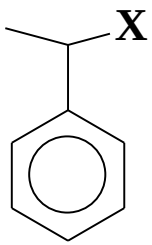
Patten, T.E., Xia, J, Abernathy, T., Matyjaszewki, K. *Science* **1996**, *272*, *866.*

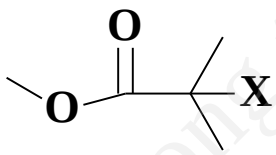
Factors affecting the molecular weight control

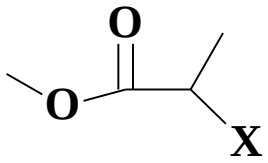


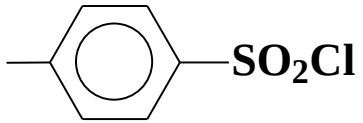
$$C\text{-}X_{Initiator} \geq C\text{-}X_{polymer}$$

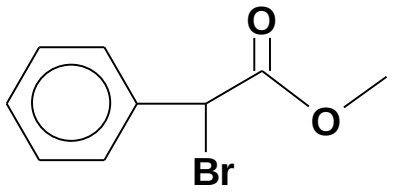
Initiator matches Monomer

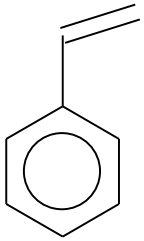


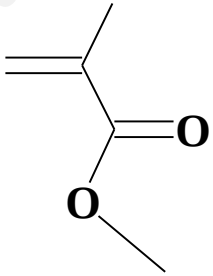


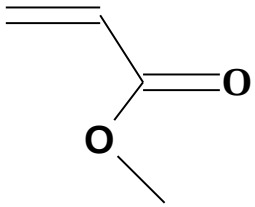








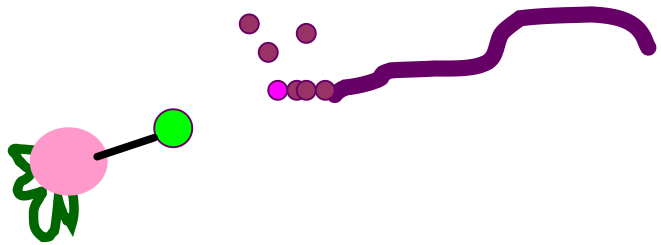




Rapid deactivation

$$\frac{M_w}{M_n} = 1 + \left(\frac{K_p[R\text{-}X]}{K_d[CuX_2]}\right)\left(\frac{2}{Conv} - 1\right)$$

$$\uparrow K_d = \frac{[CuX_2][P^{\bullet}]}{[CuX][P\text{-}X]}$$

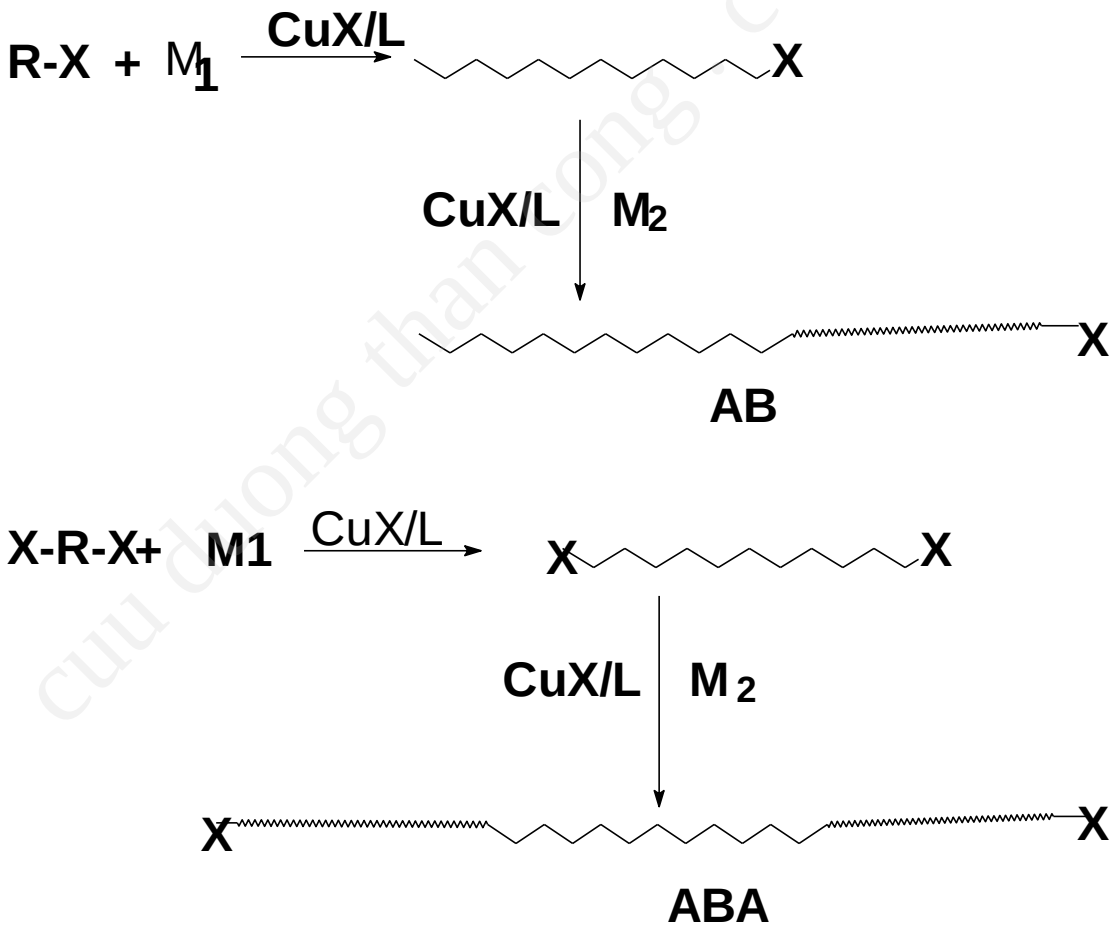


$\downarrow$ Kp - Temperature

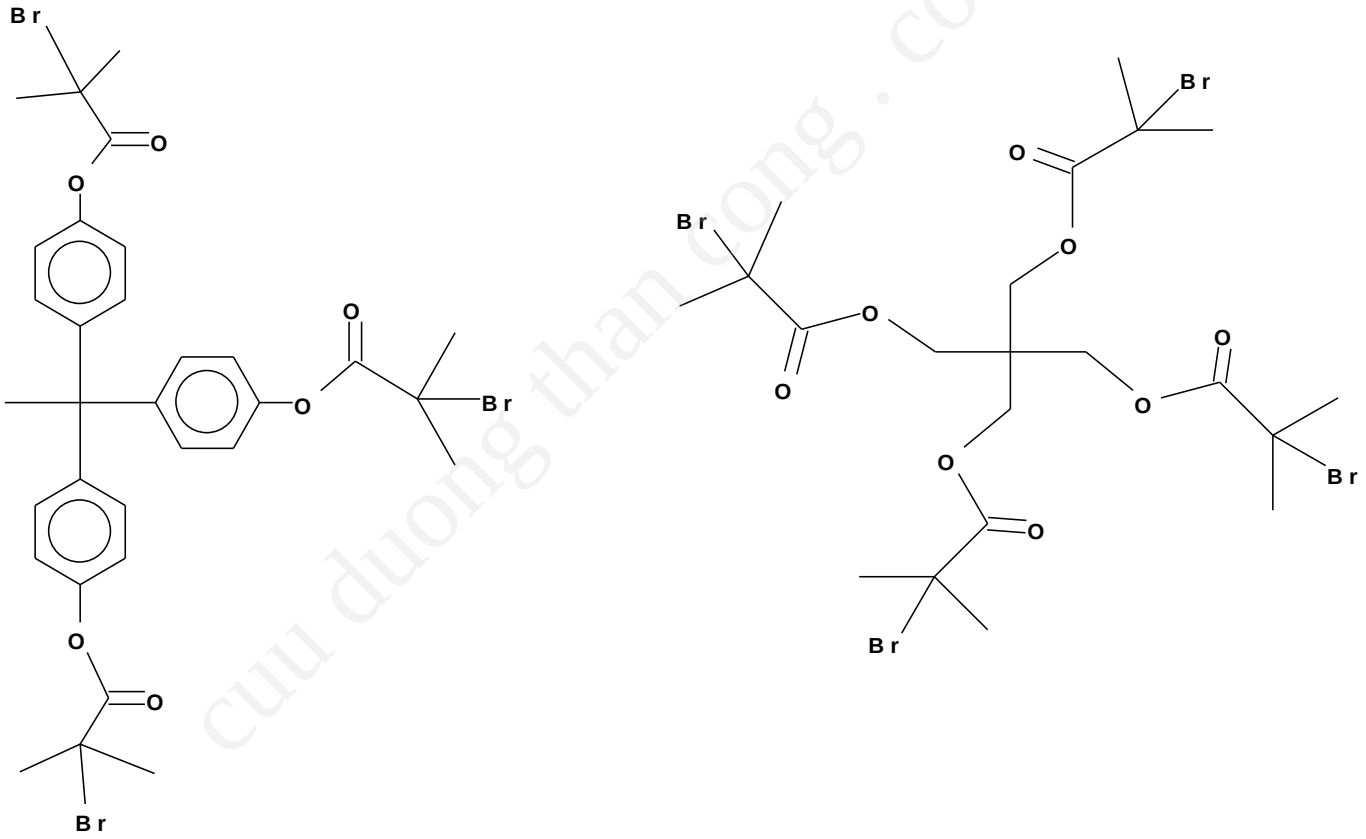
Conv.-can not go too high

B: Synthesis block copolymers

Macroinitiator method

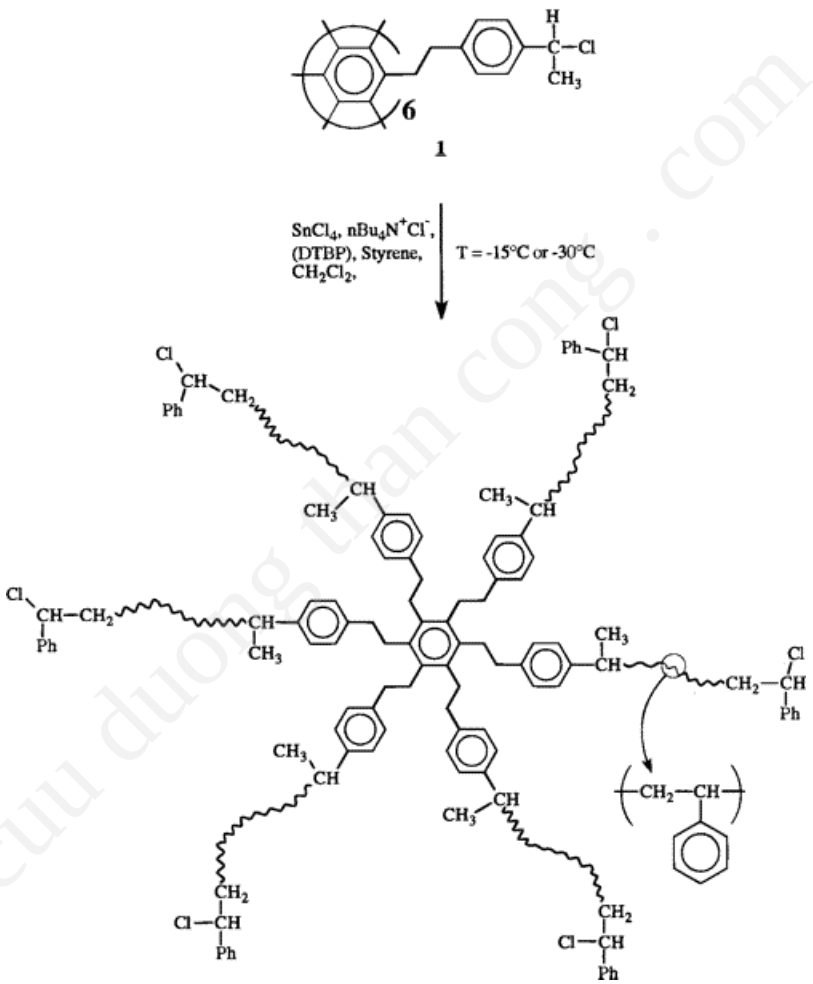


C: Synthesis of star polymers



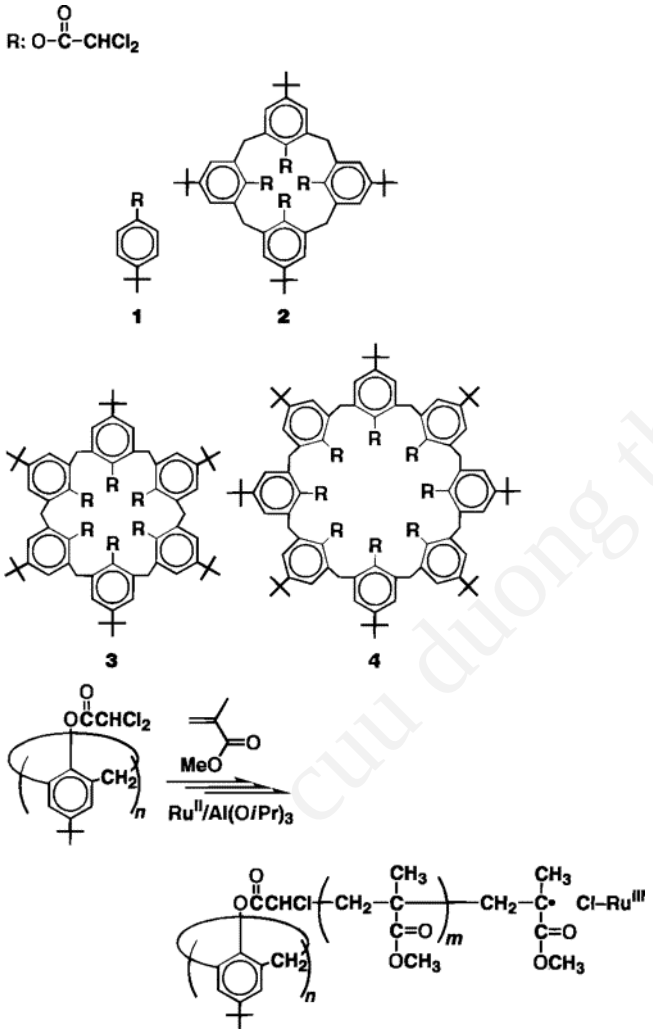
Matyjaszewski, K., Miller, P. J. Pyun, J. Kickelbick, G. Diaamanti,

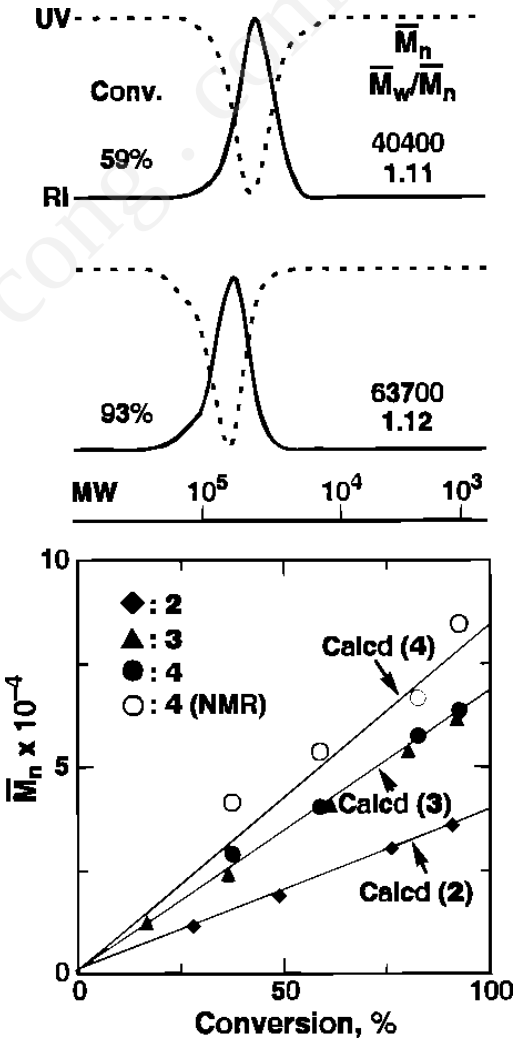
Macromolecules 1999, 32, 6526



Macromolecules, 31 (20), 6762 -6768, 1998

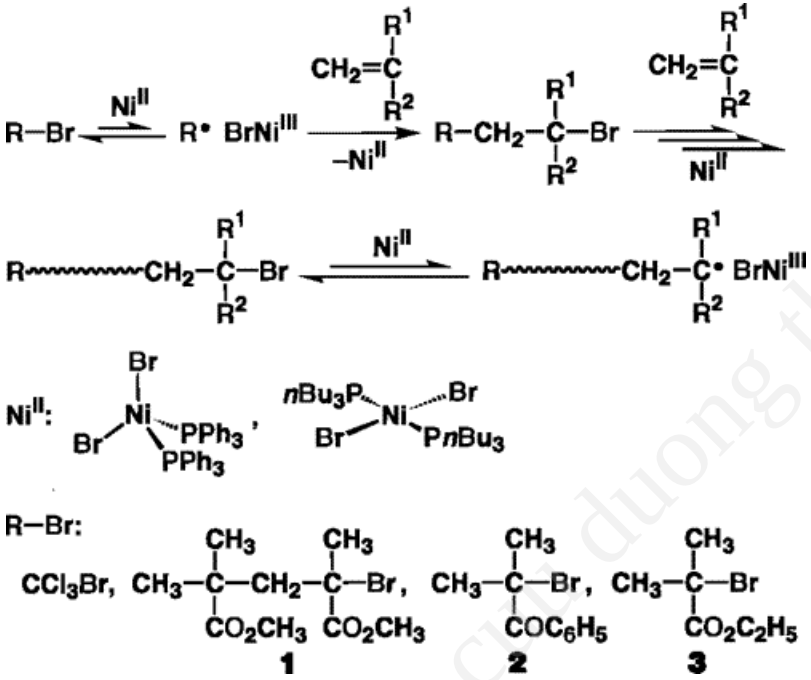
Jiro Ueda, Masami Kamigaito, and Mitsuo Sawamoto

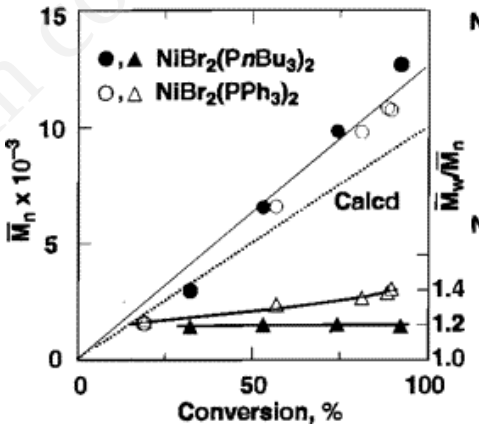


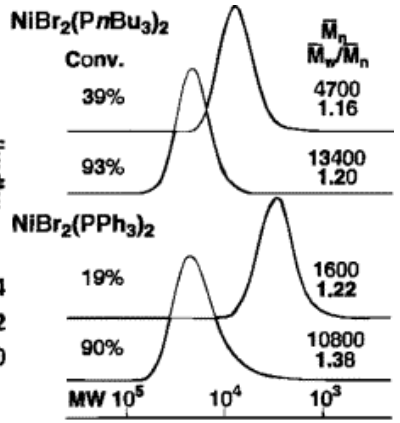


Macromolecules, 31 (20), 6756 -6761, 1998

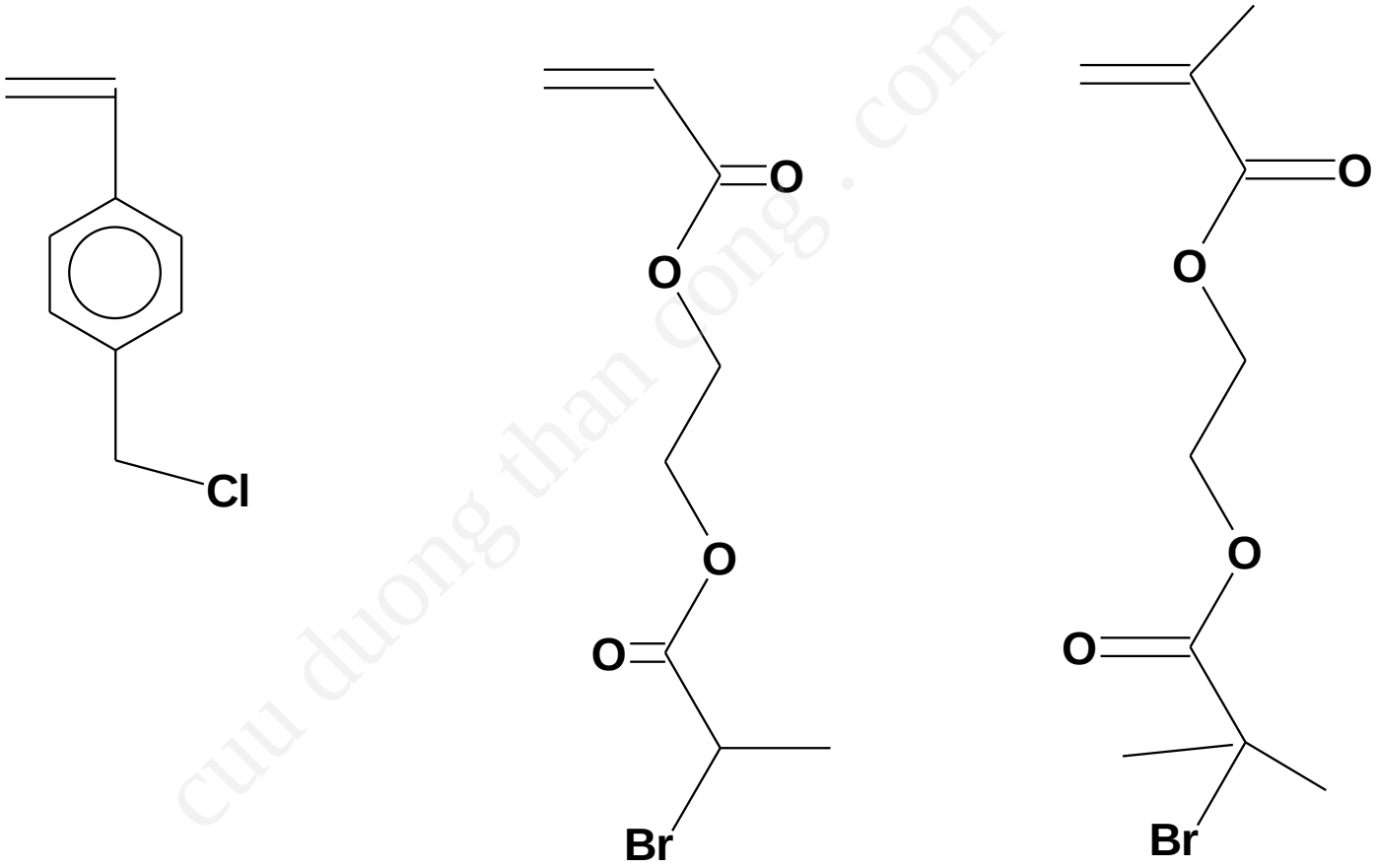
Hiroko Uegaki, Yuzo Kotani, Masami Kamigaito, and Mitsuo Sawamoto



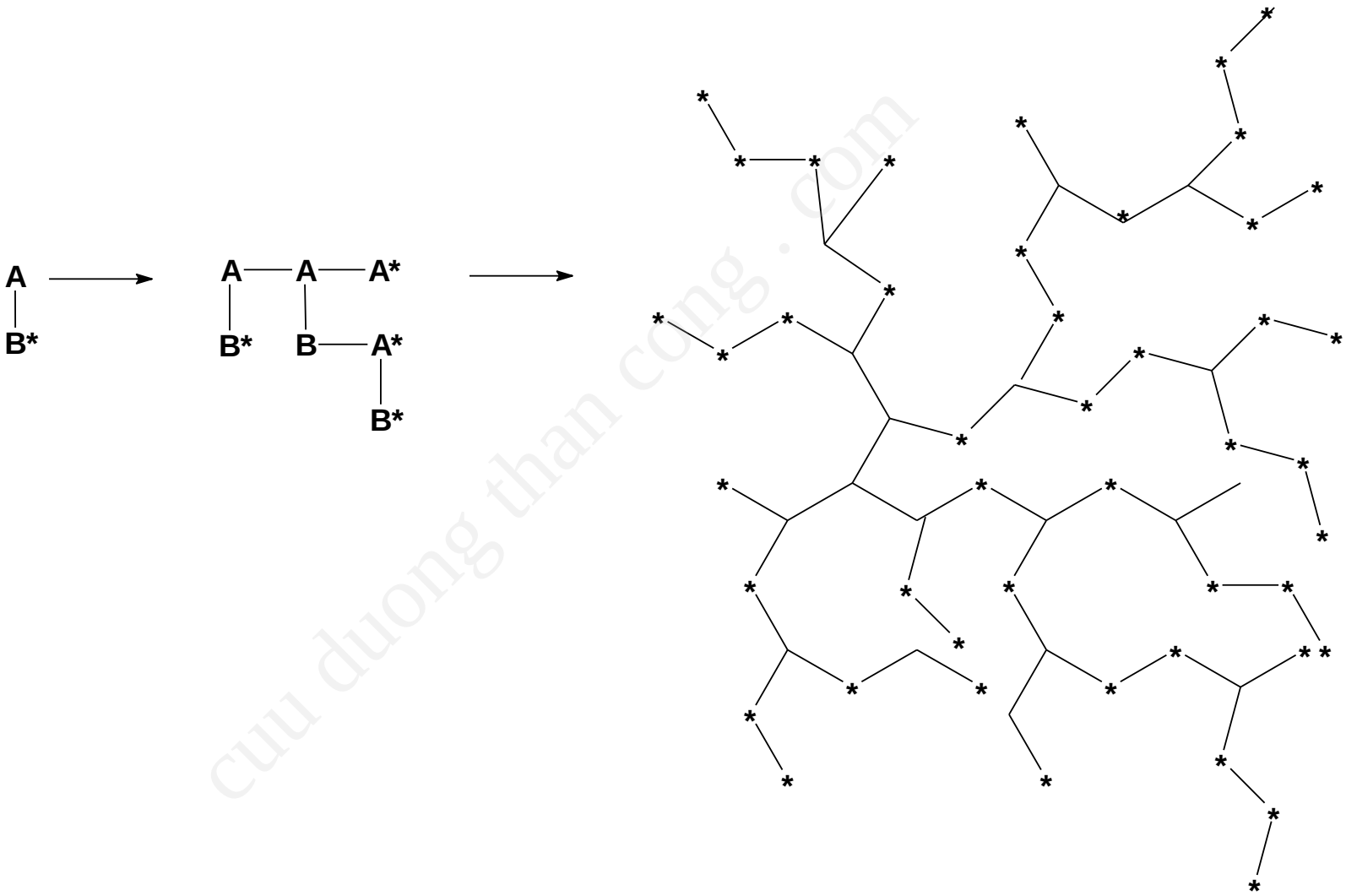




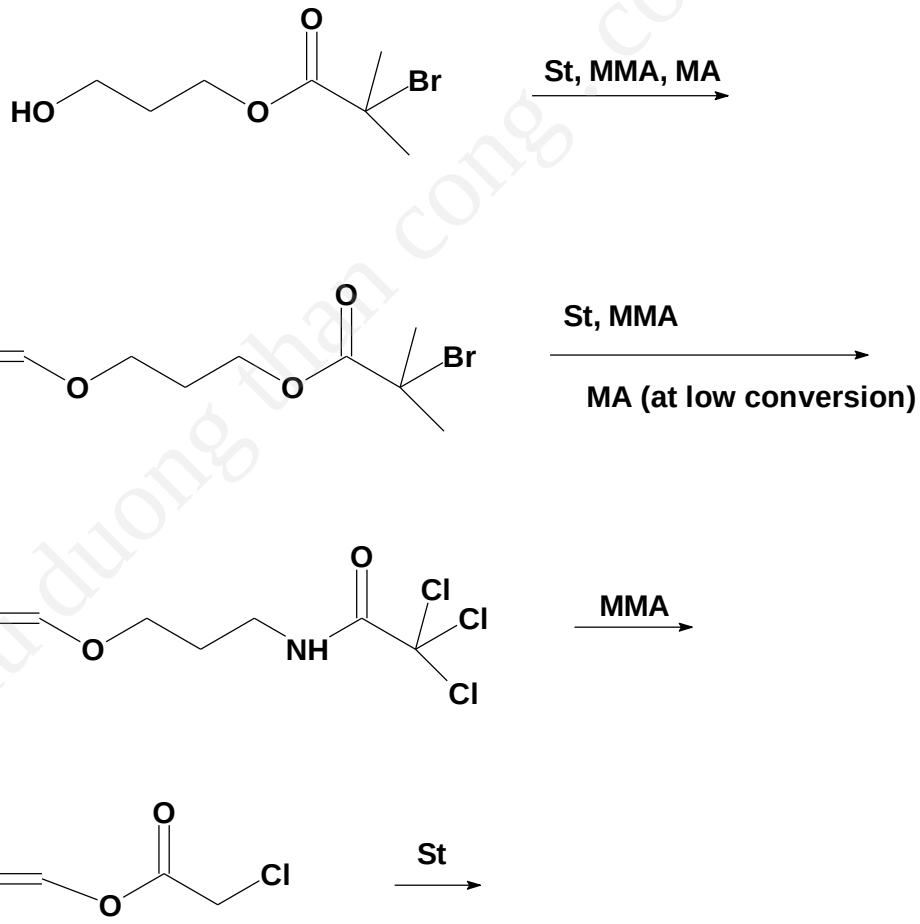
D: Hyperbranched Polymers



Monomer-Initiator

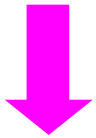


E. Synthesis of End-functionalized Polymers



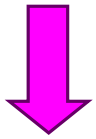
Challenges for ATRP

Low catalyst efficiency



High catalyst residual

Deep color in product



Purification

Catalyst and ligand waste

Too much "catalyst" leads to problems of cost and residual metal in products.

Rate can be accelerated;

- Reduction of copper(II) to copper(I) e.g. disproportionation with copper(0) - Matyjaszewski
- Addition of rate enhancers e.g. acid, alcohols
- Use of mildly co-ordinated solvents

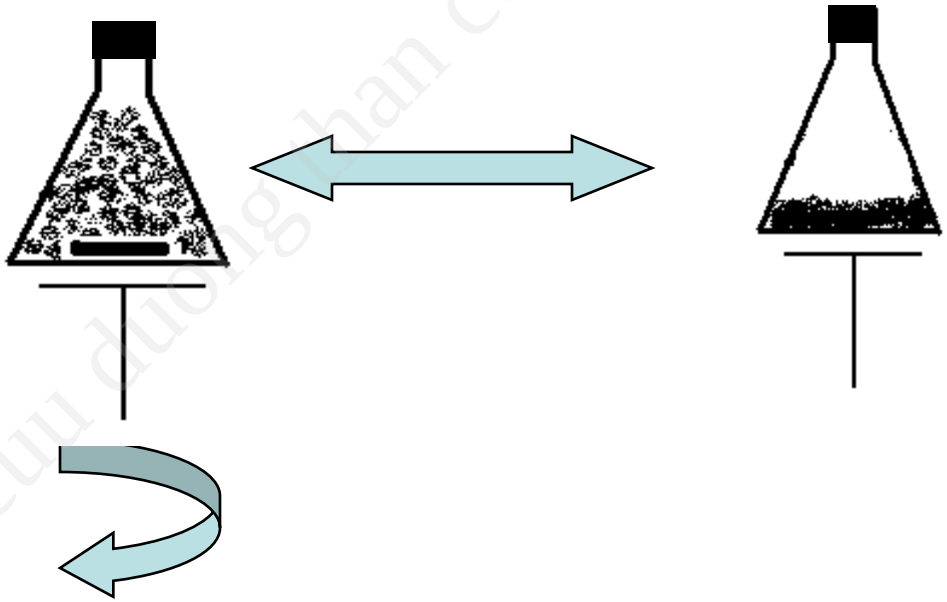
However, for many applications we require

- Much lower levels of metal
- Recycling of metal

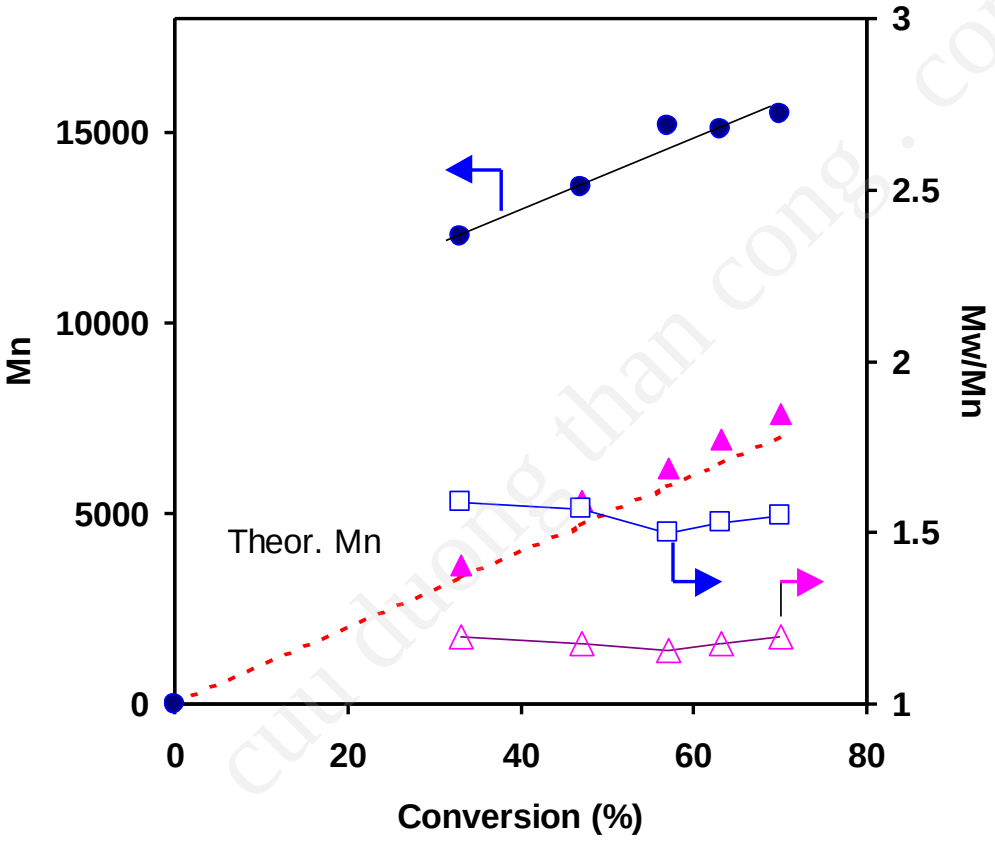
Acceptable rates of polymerisation

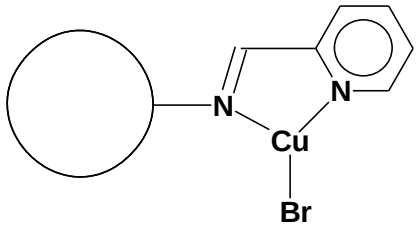
Solution to the Problem ?

- **Catalyst supporting**



Mn and PDI vs conversion in MMA polymerization by supported catalysts

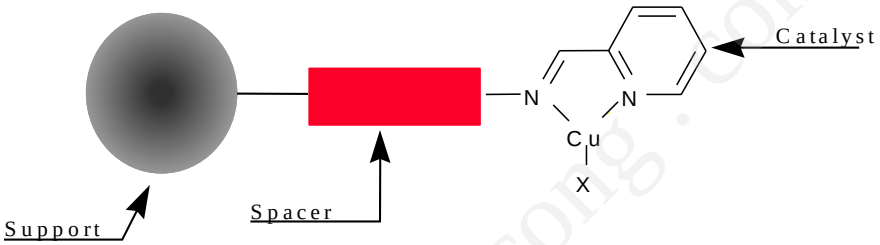


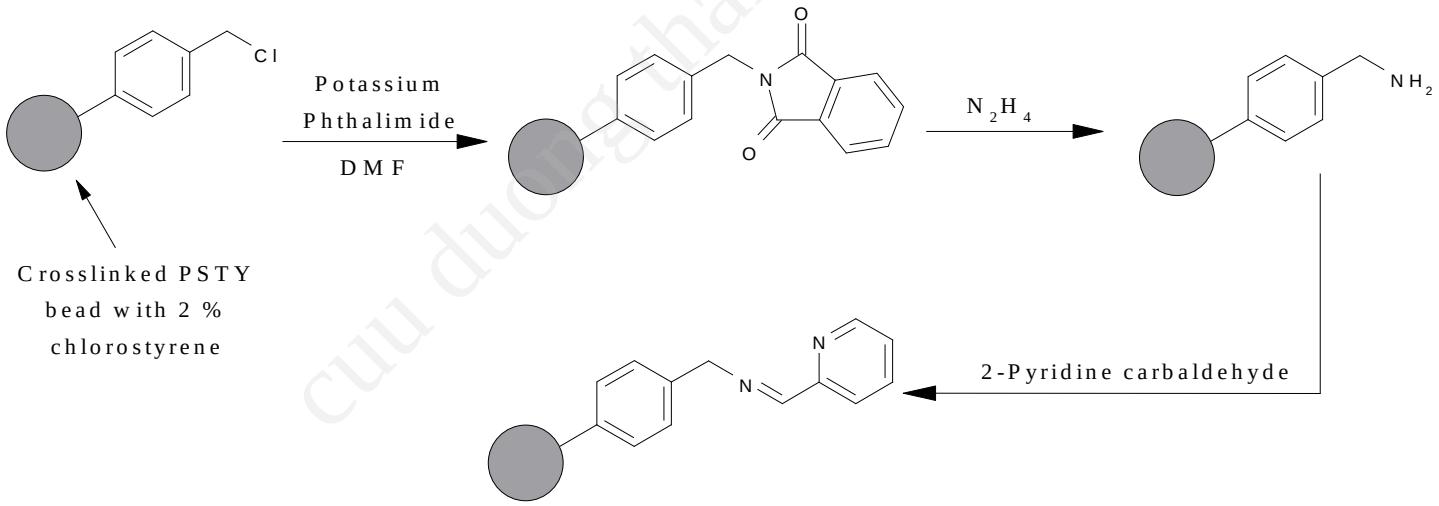


Haddleton,

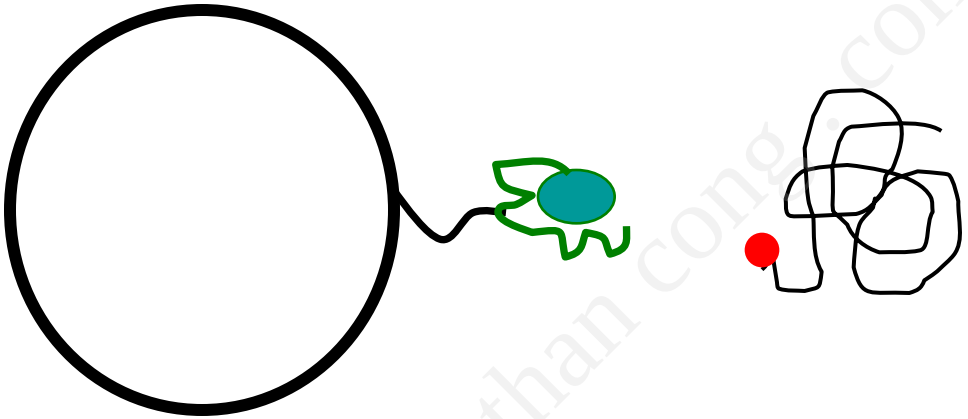
Chem. Commun. 1999, 99.

Supported catalysts for ATP





WHY?



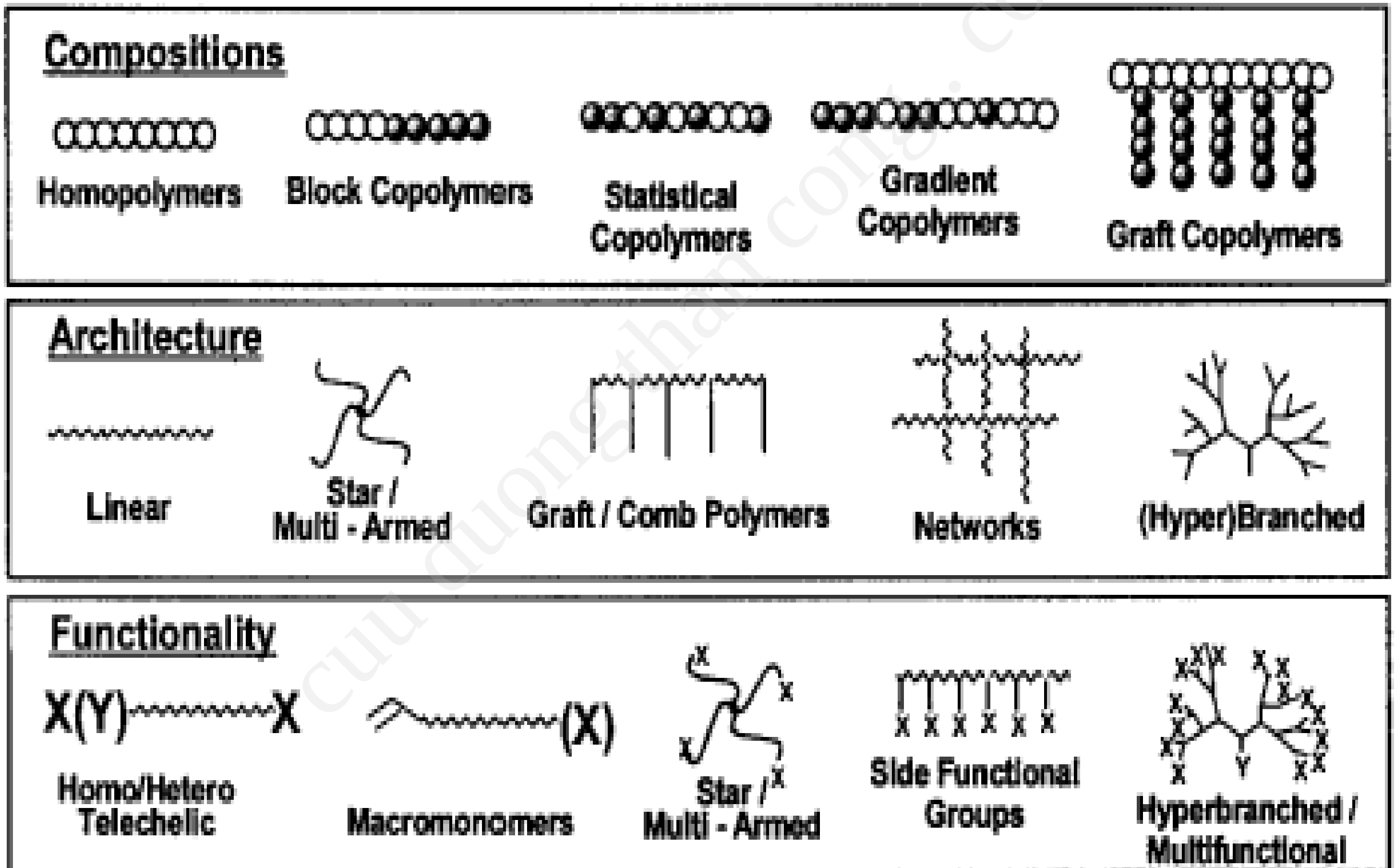
$$\frac{M_w}{M_n} = 1 + \left(\frac{K_p[R\text{-}X]}{K_d[CuX_2]}\right)\left(\frac{2}{Conv} - 1\right)$$

Future development

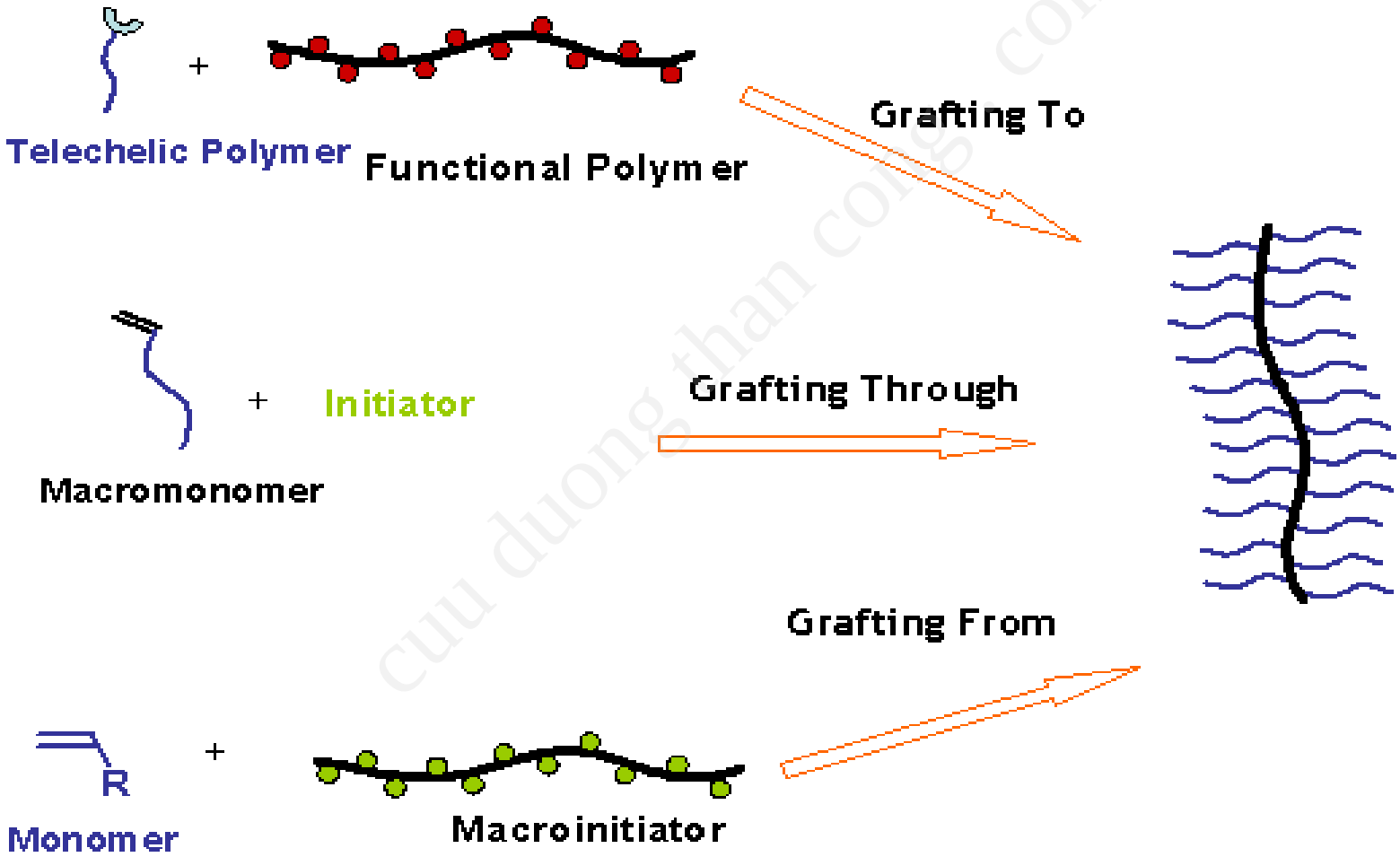
- Develop high reactive catalysts

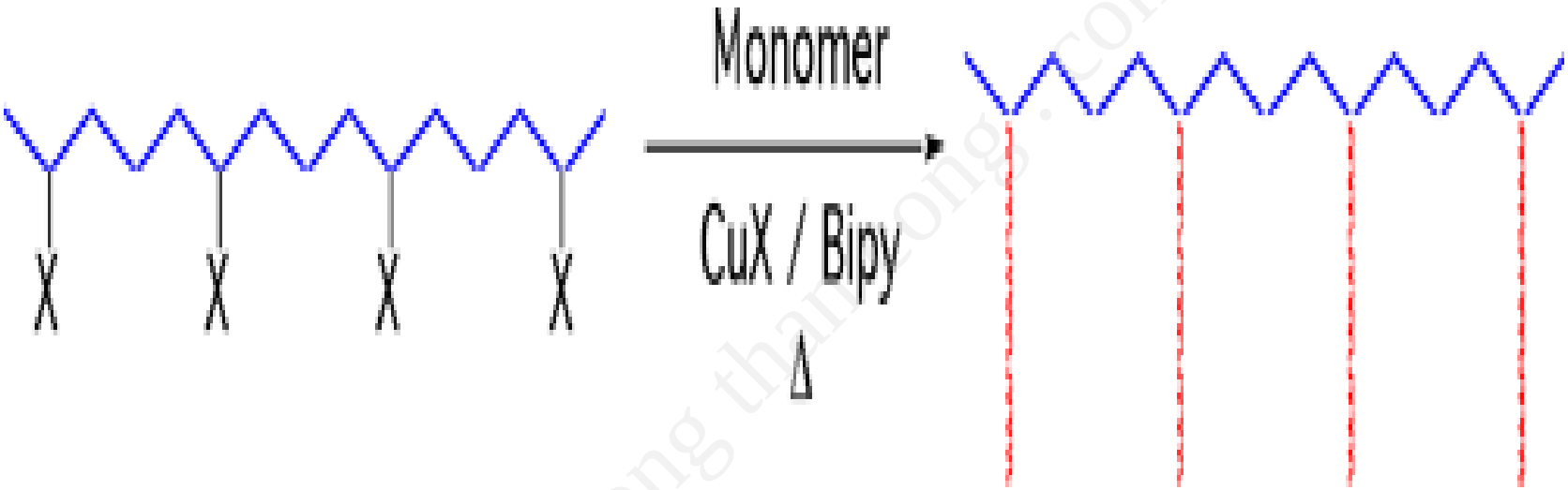
What Can Living Polymerizations Do?

$DP_n = \Delta[M]/[I]_o$; $200 < M_n < 200{,}000$; $1.04 < M_w/M_n < 1.3$

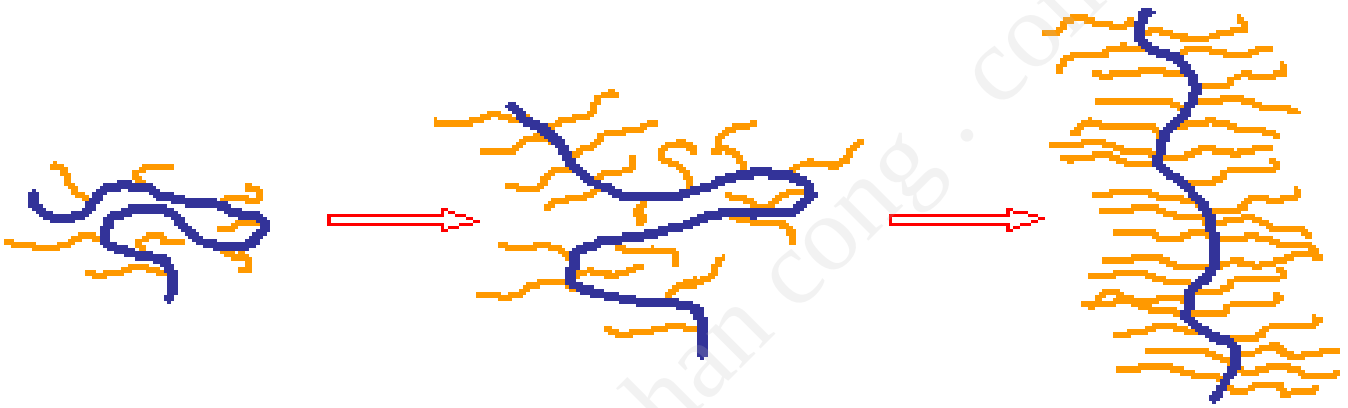


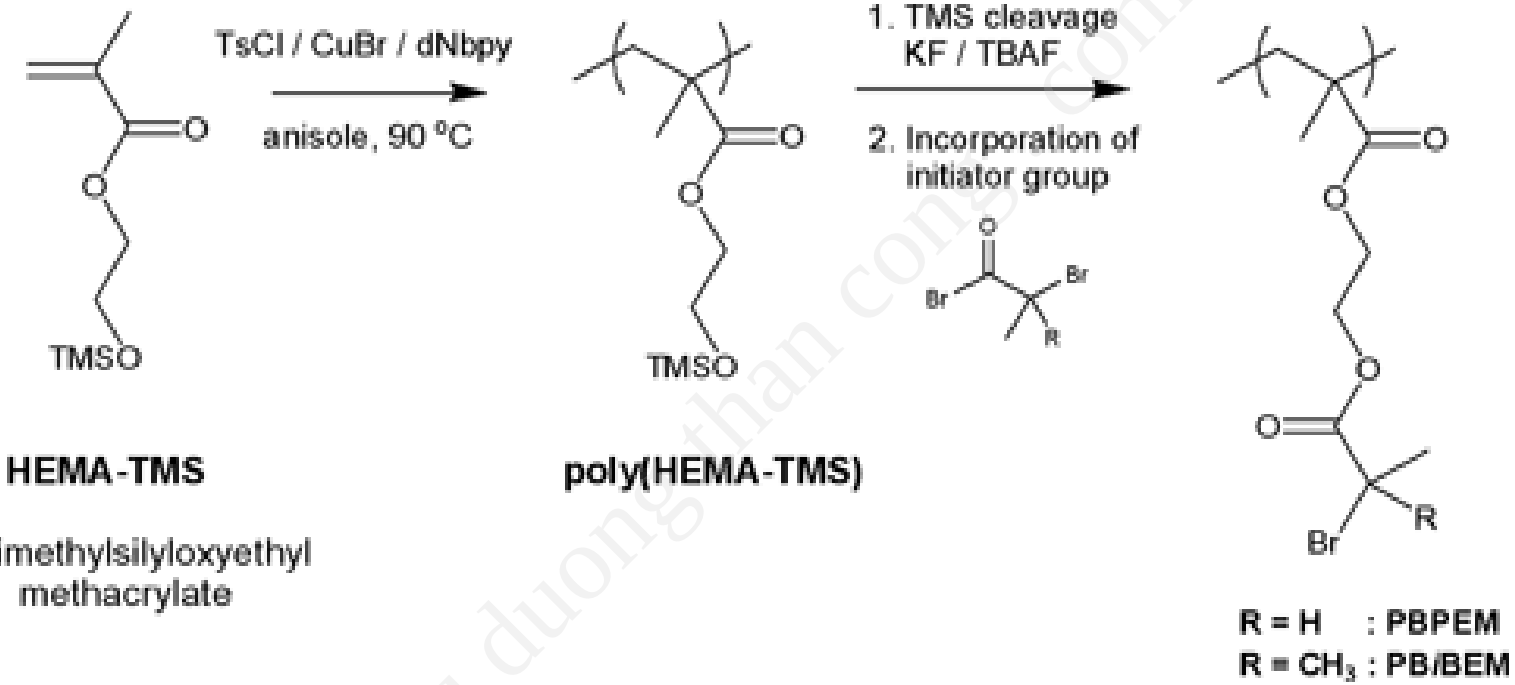
Graft Copolymers





Brush Copolymer

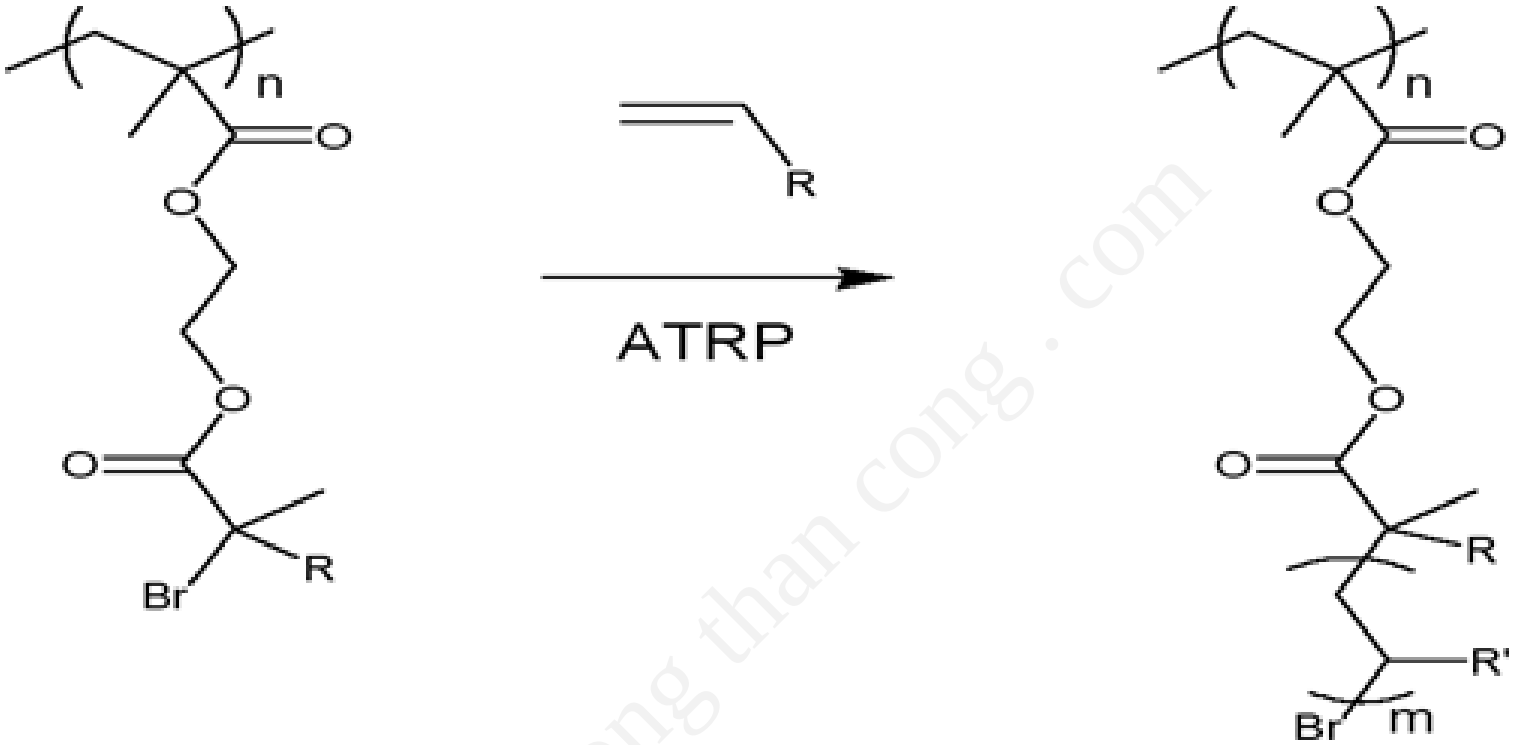




HEMA-TMS

2-trimethylsilyloxyethyl methacrylate

poly(HEMA-TMS)



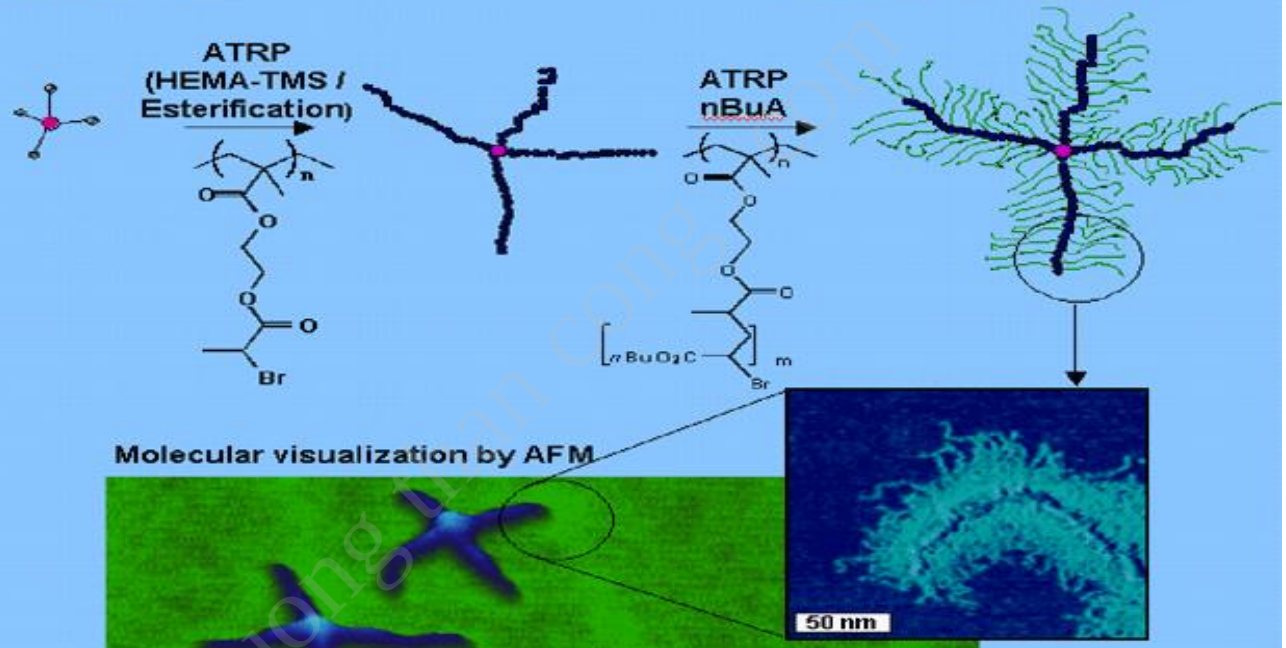
http://pubs.acs.org/Macromolecules

MAMOBx

Macromolecules

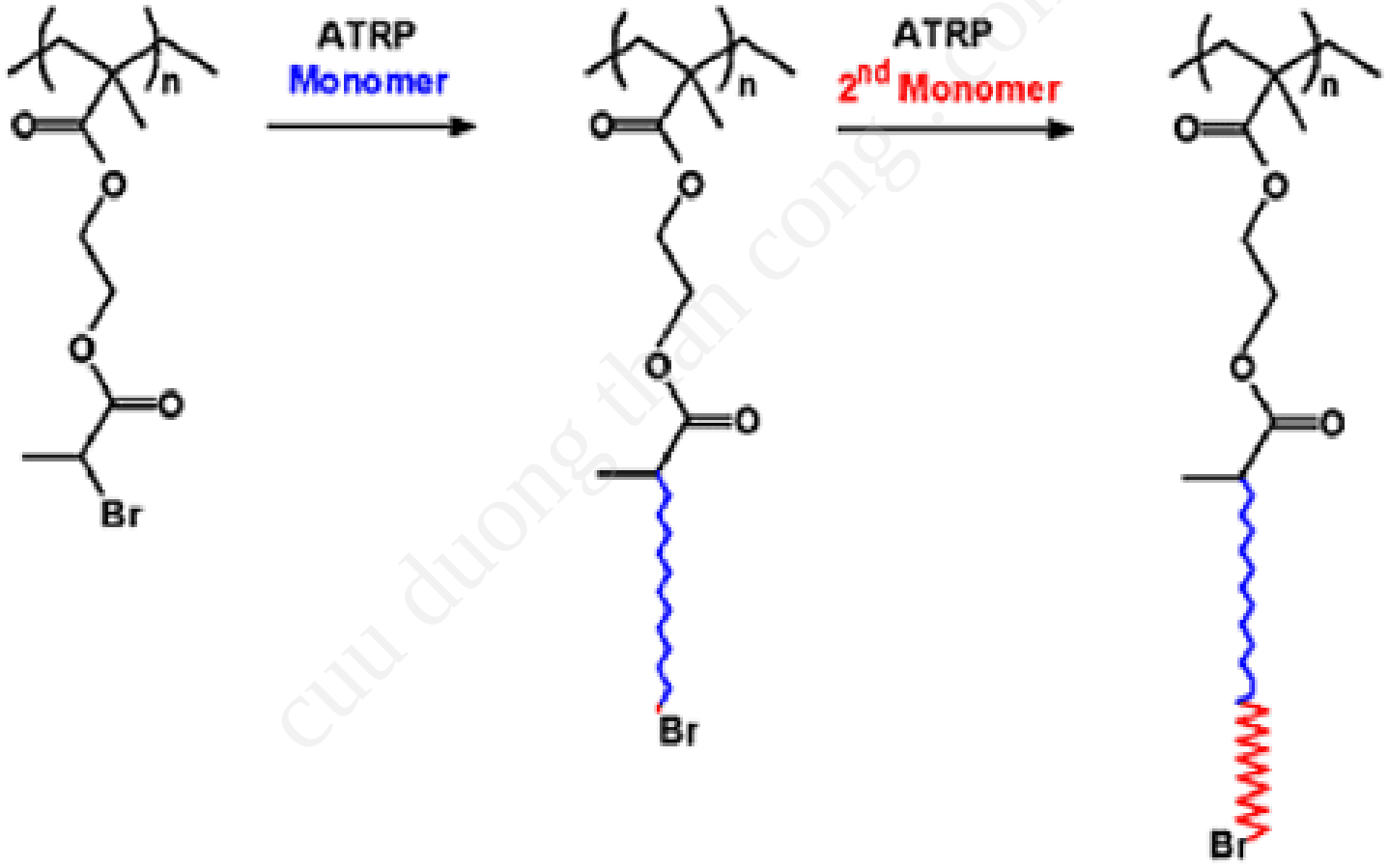
OCTOBER 7, 2003

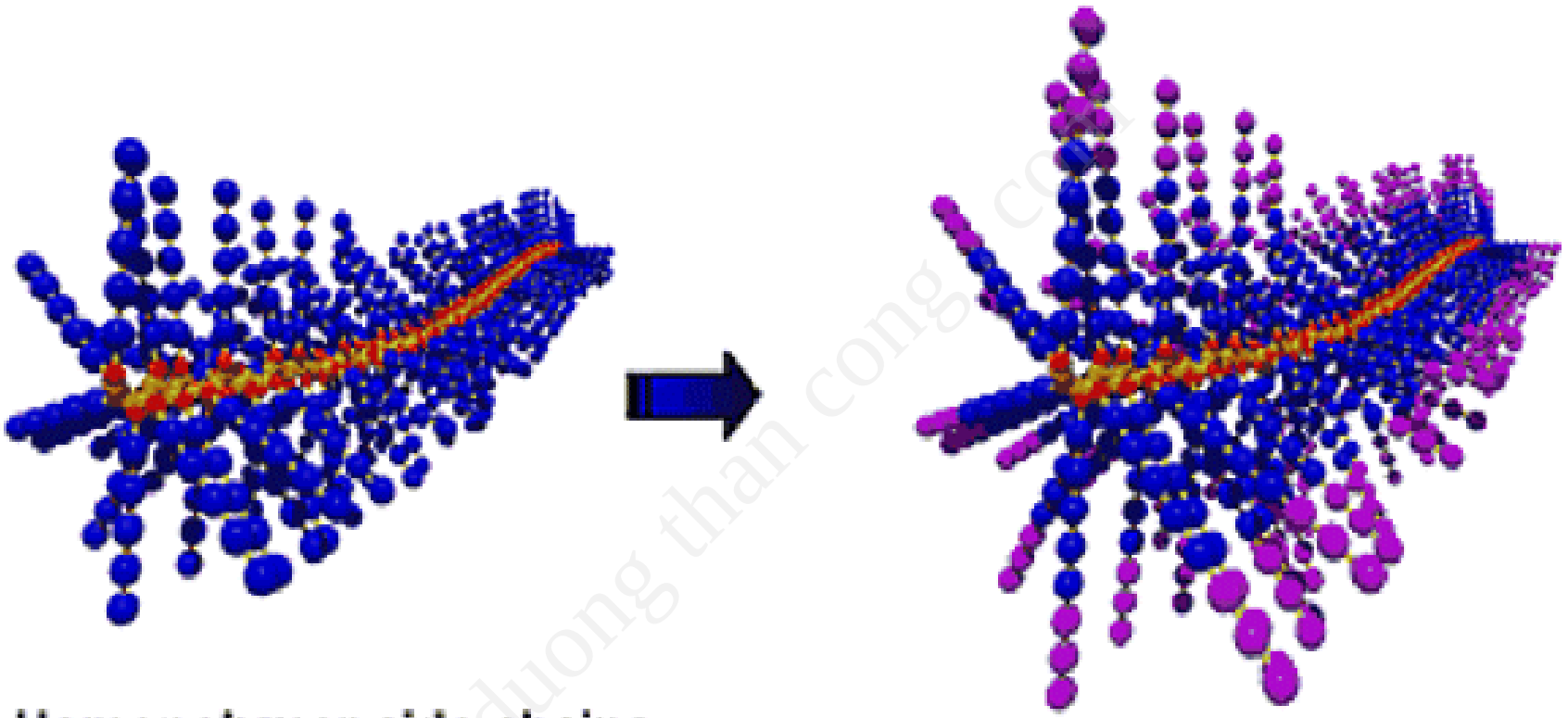
VOLUME 36, Number 22



A PUBLICATION OF THE AMERICAN CHEMICAL SOCIETY

Block copolymer side chains





Homopolymer side chains

Block copolymer side chains

Synthesis, characterization and application of well-defined environmentally responsive polymer brushes on the surface of colloid particles

Mingming Zhang [a], Li Liu [a,*], Chenglin Wu [a], Guoqi Fu [a], Hanying Zhao [b], Binglin He [a]

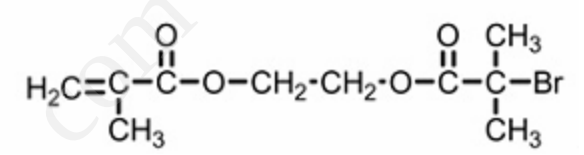
[a] *Key Laboratory of Functional Polymer Materials, Ministry of Education, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, PR China*

[b] *Department of Chemistry, College of Chemistry, Nankai University, Tianjin 300071, PR China*

Polymer 48 (2007) 1989–1997

Materials

2-(2-Bromoisobutyryloxy) ethyl methacrylate (BIEM)



2-(Dimethylamino) ethyl methacrylate (DMAEMA)

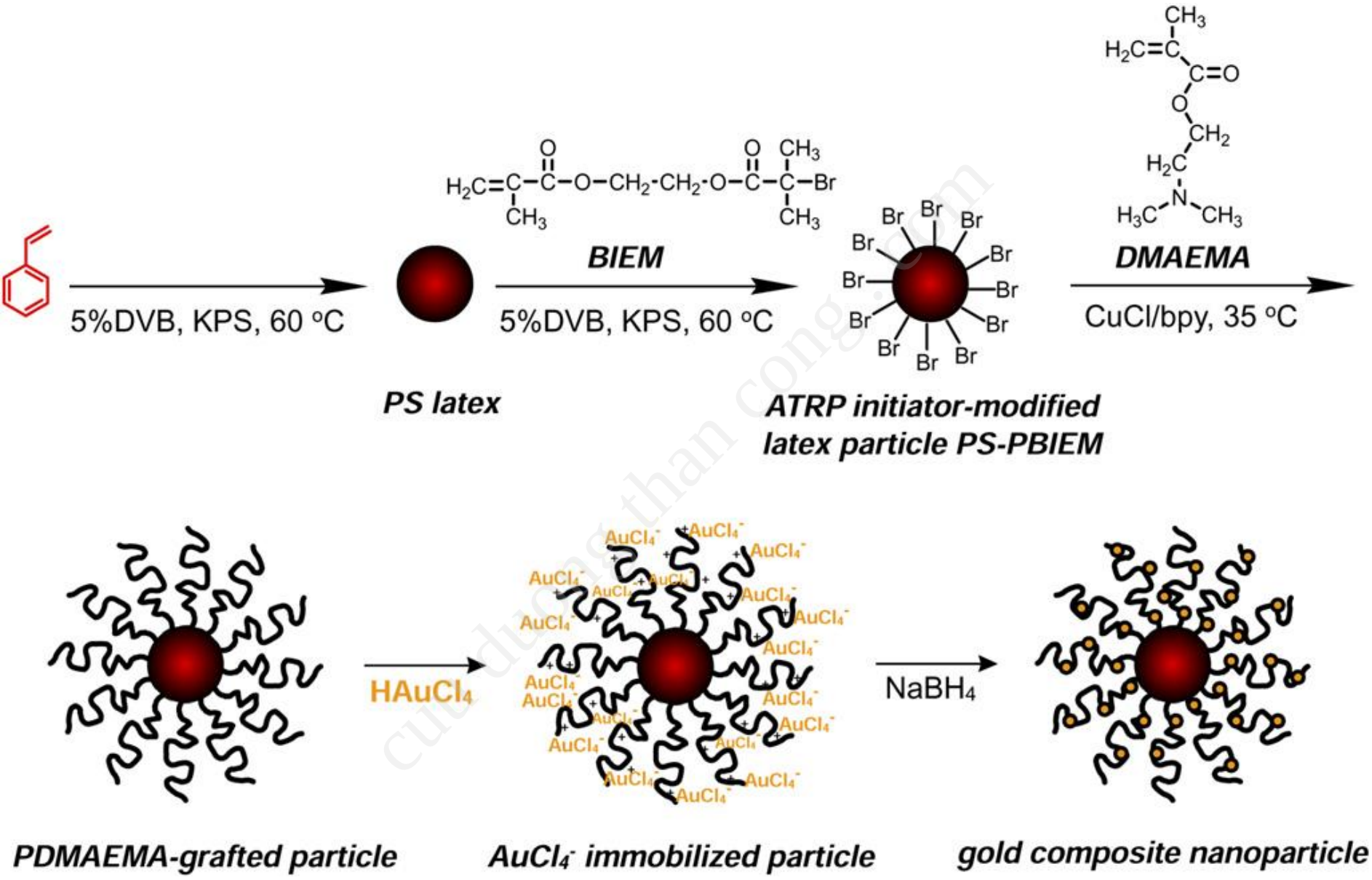
Hydroxylethyl methacrylate (HEMA)

Ethyl -2-bromoisobutyrate

HAuCl4,4H2O

NaBH4

Potassium persulfate (KPS)



Synthesis of PDMAEMA brushes on the surface of colloid particles by ATRP.

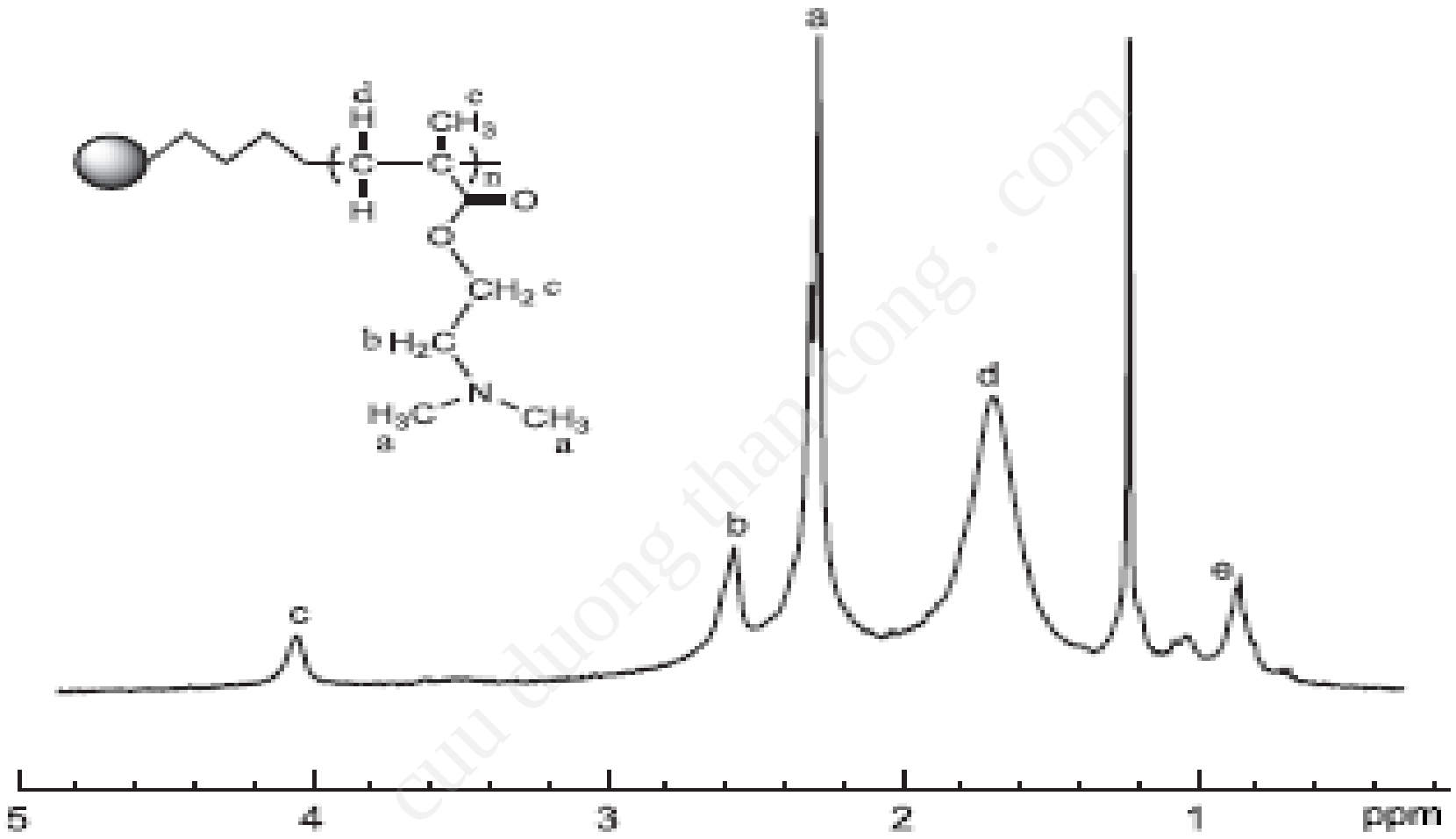
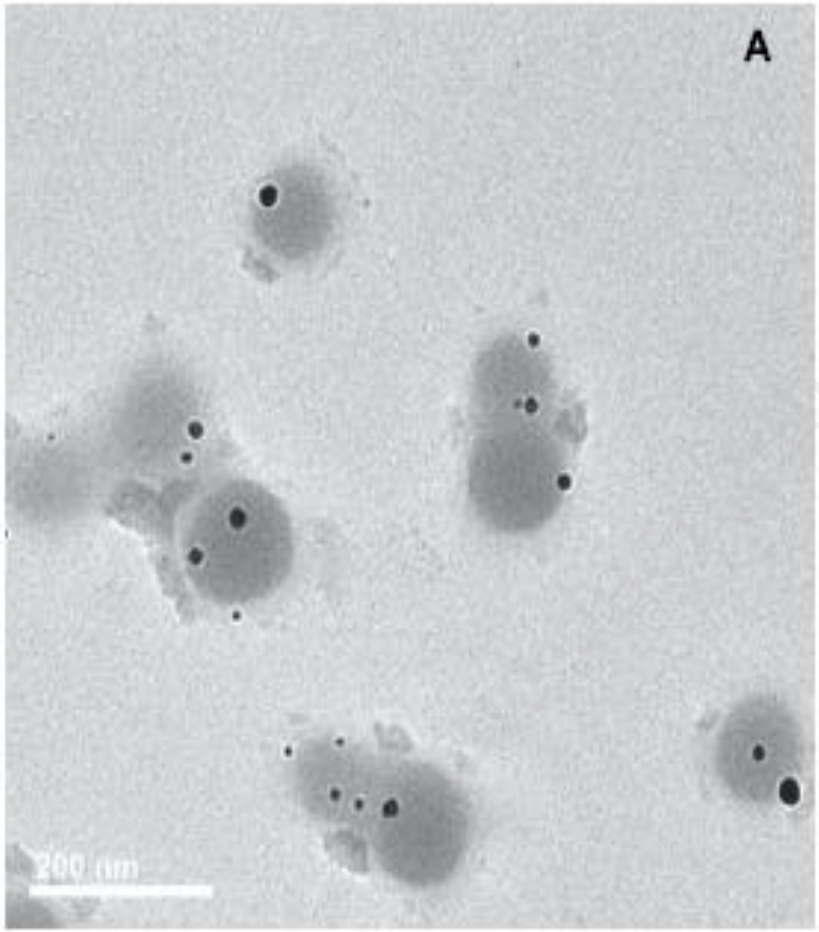
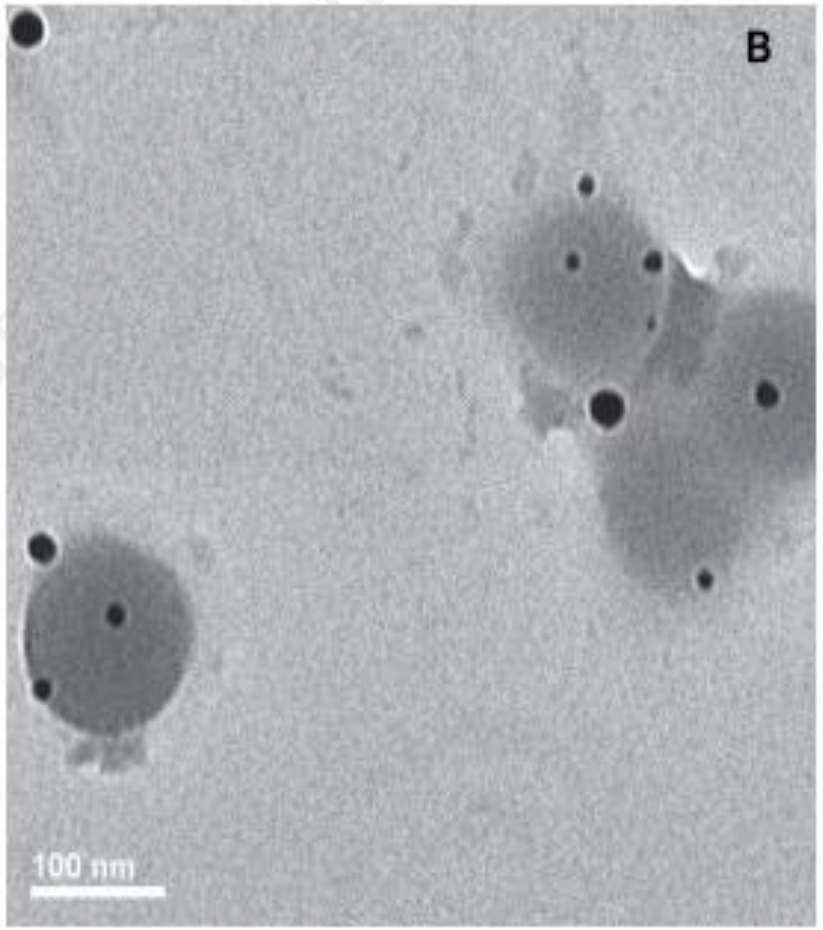
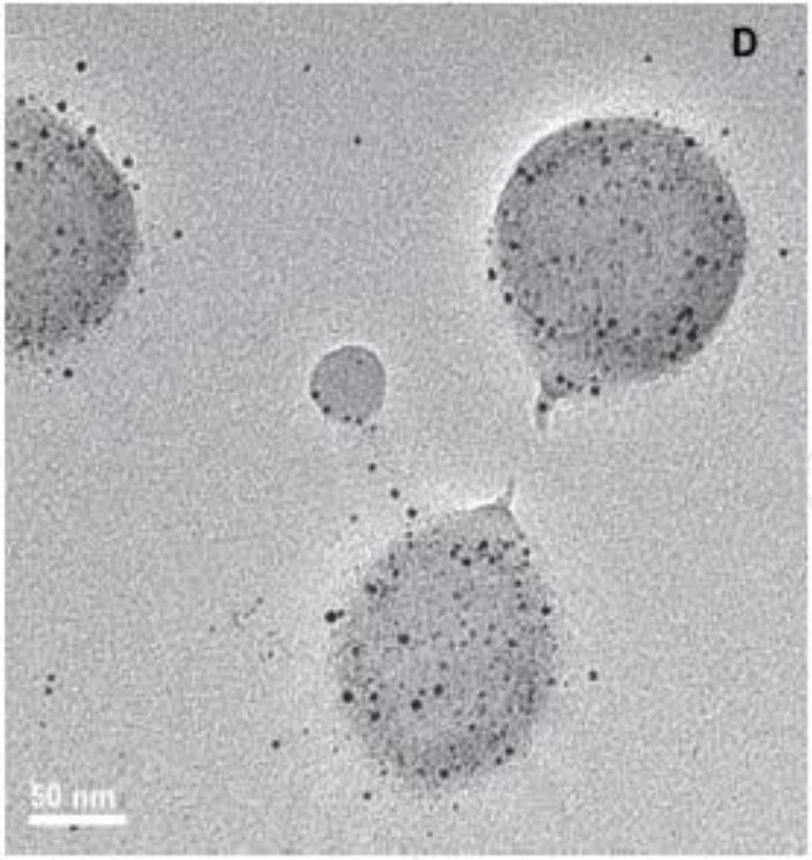


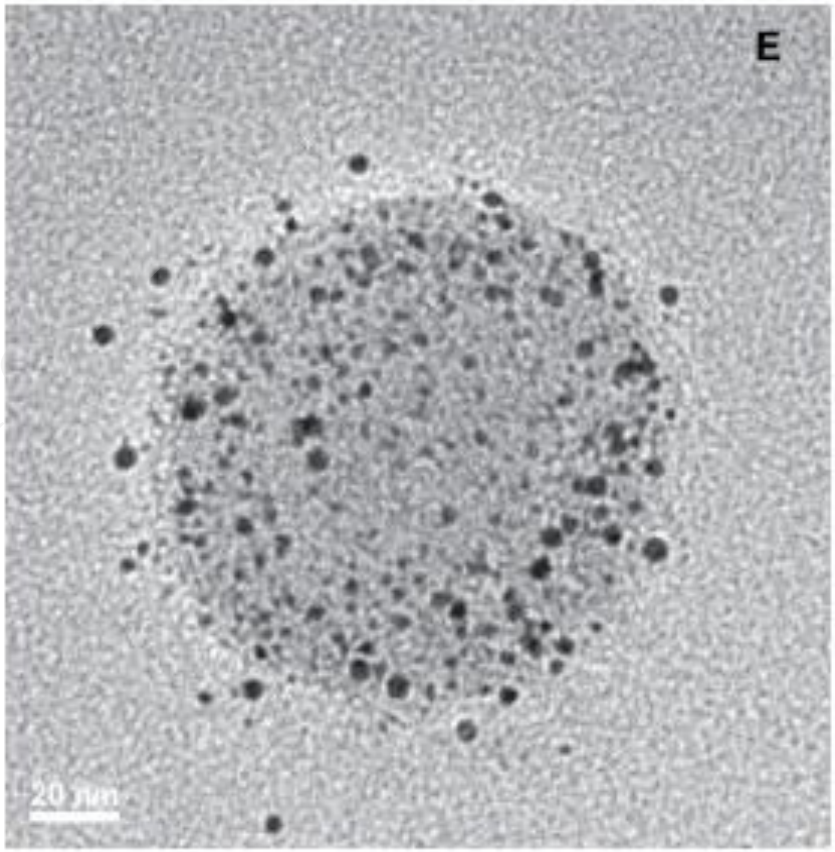
Fig. 1. ^{1}H NMR spectrum of PDMAEMA-grafted particles in $CDCl_3$.

TEM images of the gold composite nanoparticles prepared without (A, B) and with adding $NaBH_4$ (D, E)

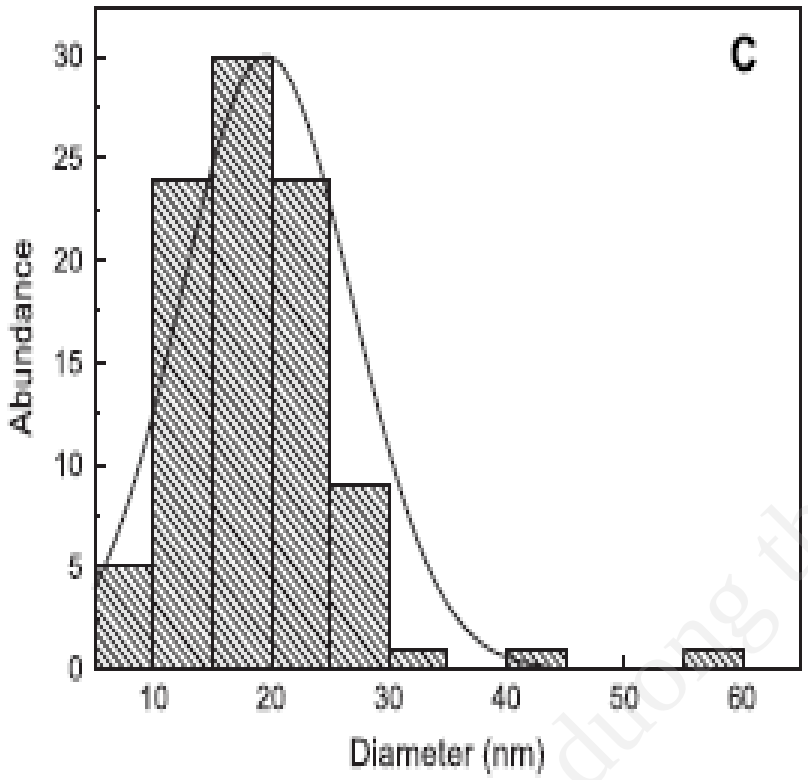


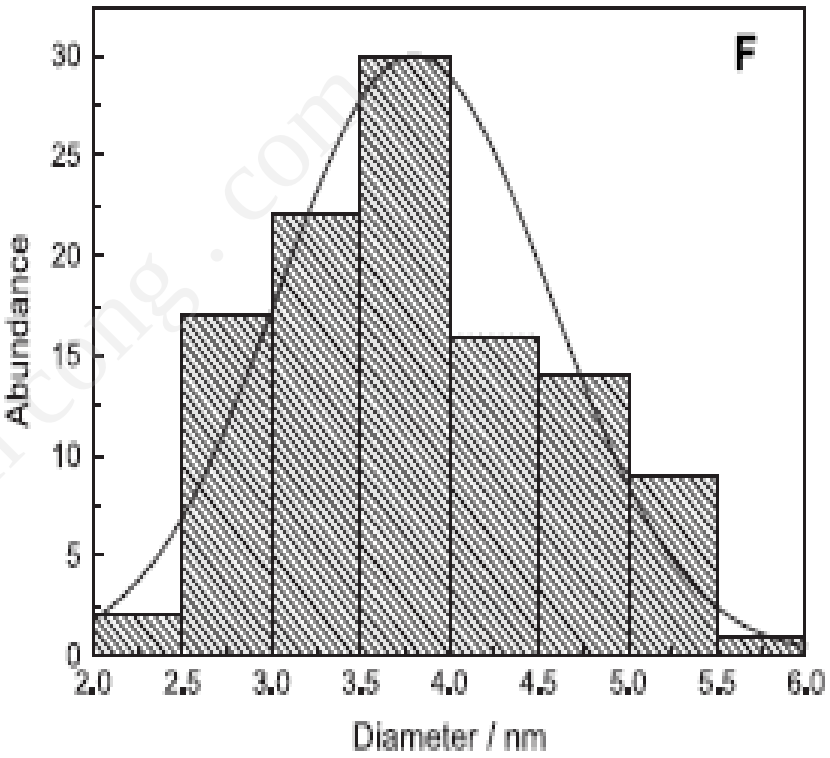


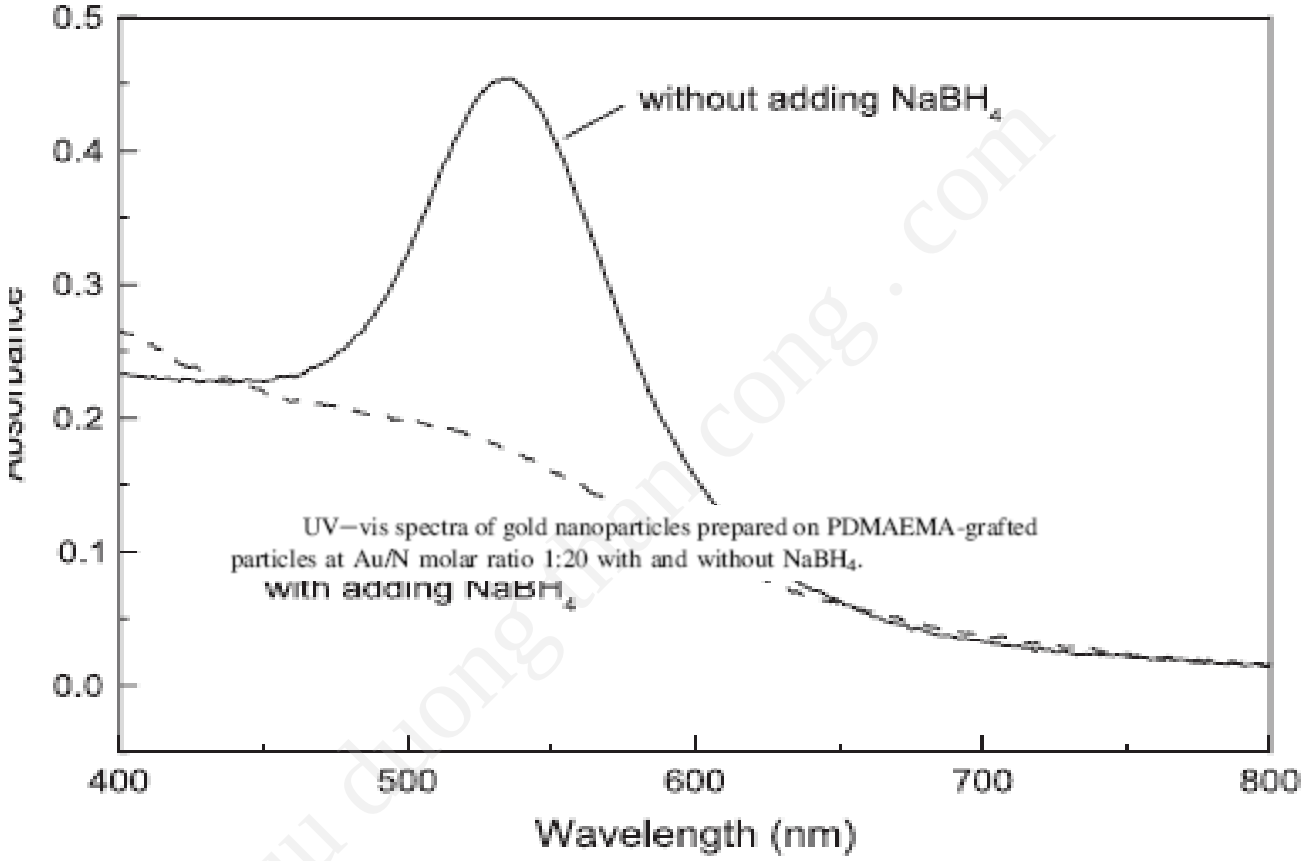




size distributions







UV–vis spectra of gold nanoparticles prepared on PDMAEMA-grafted particles at Au/N molar ratio 1:20 with and without $NaBH_4$.

UV–vis spectra of gold nanoparticles prepared on PDMAEMA-grafted particles at Au/N molar ratio 1:20 with and without $NaBH_4$.