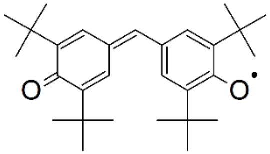
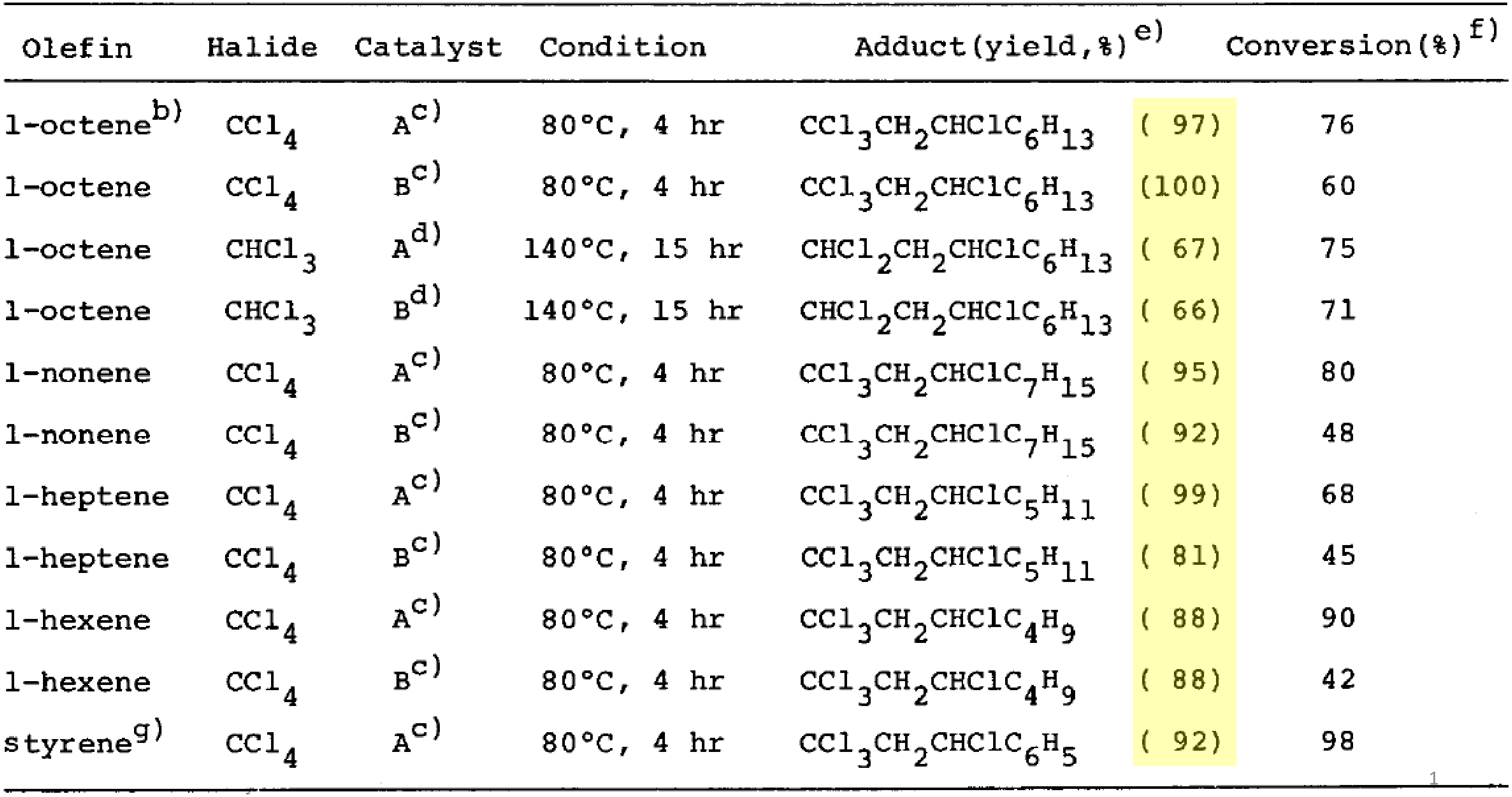
Atom Transfer Radical Polymerization

***prequel**: addition of alkyl-halides to olefins catalyzed by transition metal complexes*



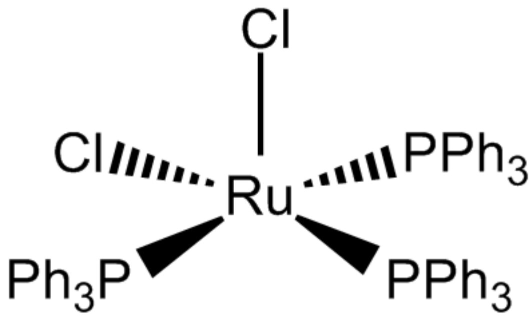
galvinoxyl (radical inhibitor)

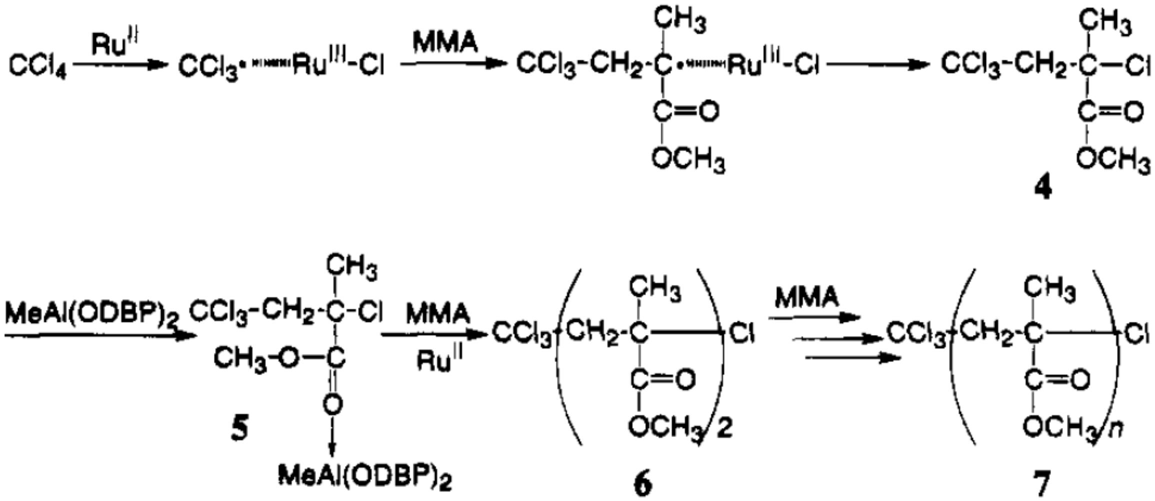


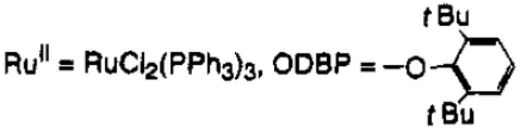
Olefin	Halide	Catalyst	Condition	Adduct (yield, %)[e]		Conversion (%)[f]
1-octene[b]	CCl_4	A[c]	80°C, 4 hr	$CCl_3CH_2CHClC_6H_{13}$	(97)	76
1-octene	CCl_4	B[c]	80°C, 4 hr	$CCl_3CH_2CHClC_6H_{13}$	(100)	60
1-octene	$CHCl_3$	A[d]	140°C, 15 hr	$CHCl_2CH_2CHClC_6H_{13}$	(67)	75
1-octene	$CHCl_3$	B[d]	140°C, 15 hr	$CHCl_2CH_2CHClC_6H_{13}$	(66)	71
1-nonene	CCl_4	A[c]	80°C, 4 hr	$CCl_3CH_2CHClC_7H_{15}$	(95)	80
1-nonene	CCl_4	B[c]	80°C, 4 hr	$CCl_3CH_2CHClC_7H_{15}$	(92)	48
1-heptene	CCl_4	A[c]	80°C, 4 hr	$CCl_3CH_2CHClC_5H_{11}$	(99)	68
1-heptene	CCl_4	B[c]	80°C, 4 hr	$CCl_3CH_2CHClC_5H_{11}$	(81)	45
1-hexene	CCl_4	A[c]	80°C, 4 hr	$CCl_3CH_2CHClC_4H_9$	(88)	90
1-hexene	CCl_4	B[c]	80°C, 4 hr	$CCl_3CH_2CHClC_4H_9$	(88)	42
styrene[g]	CCl_4	A[c]	80°C, 4 hr	$CCl_3CH_2CHClC_6H_5$	(92)	98

Atom Transfer Radical Polymerization (ATRP)

*M. Sawamoto, Macromolecules 28, 1721 (**1995**)*







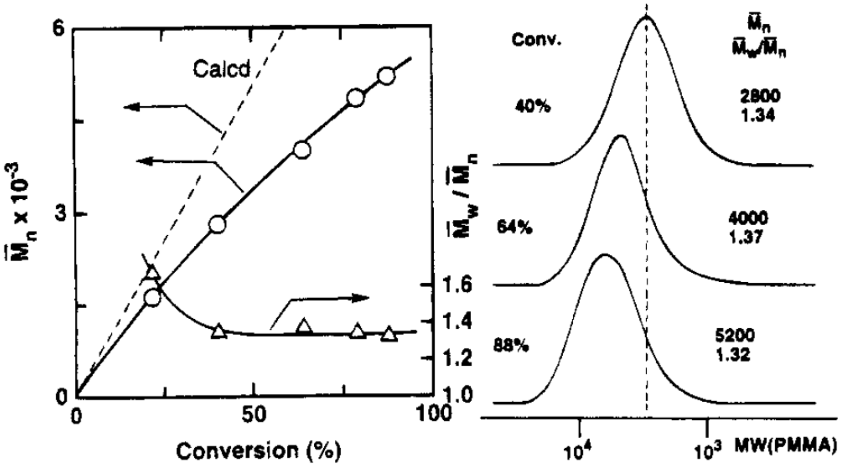
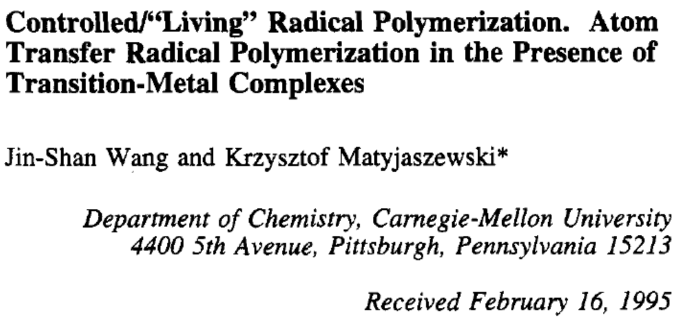


Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained with $CCl_4/RuCl_2(PPh_3)_3/MeAl(ODBP)_2$ in toluene at 60 °C: $[MMA]_0 = 2.0$ M; $[CCl_4]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[MeAl(ODBP)_2]_0 = 40$ mM.



Controlled/“Living” Radical Polymerization. Atom Transfer Radical Polymerization in the Presence of Transition-Metal Complexes

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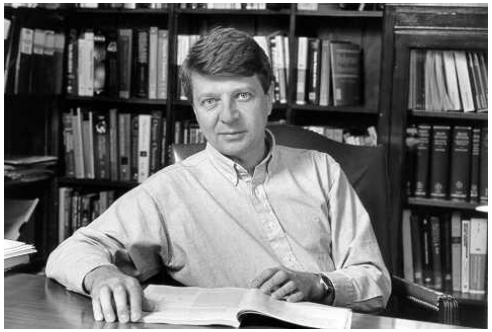
Received February 16, 1995



Prof. Krzysztof Matyjaszewski
Carnegie Mellon University

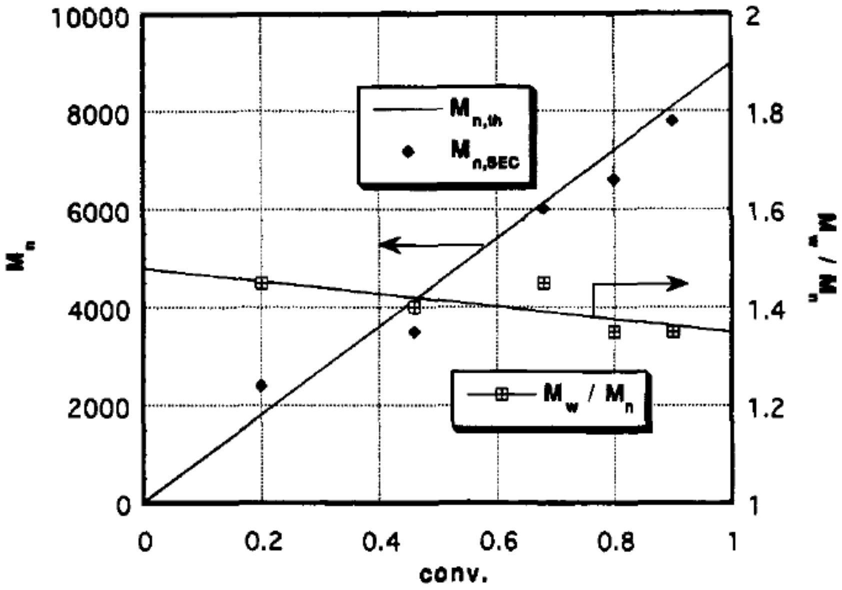


Figure 1. Dependence of molecular weights and polydispersities on conversion in bulk polymerization of styrene at 130 °C with $[1\text{-PECl}]_0 = 0.1$ mol/L, $[CuCl]_0 = 0.1$ mol/L, $[bpy]_0 = 0.3$ mol/L.

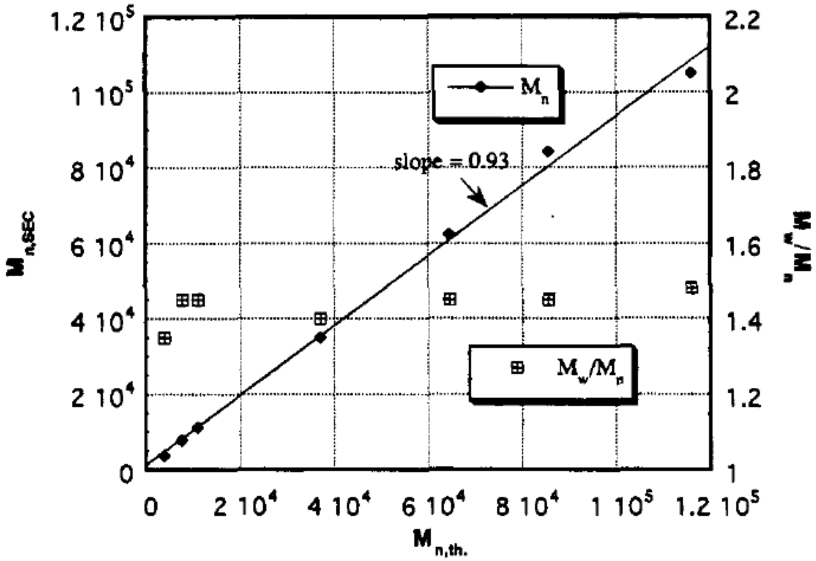
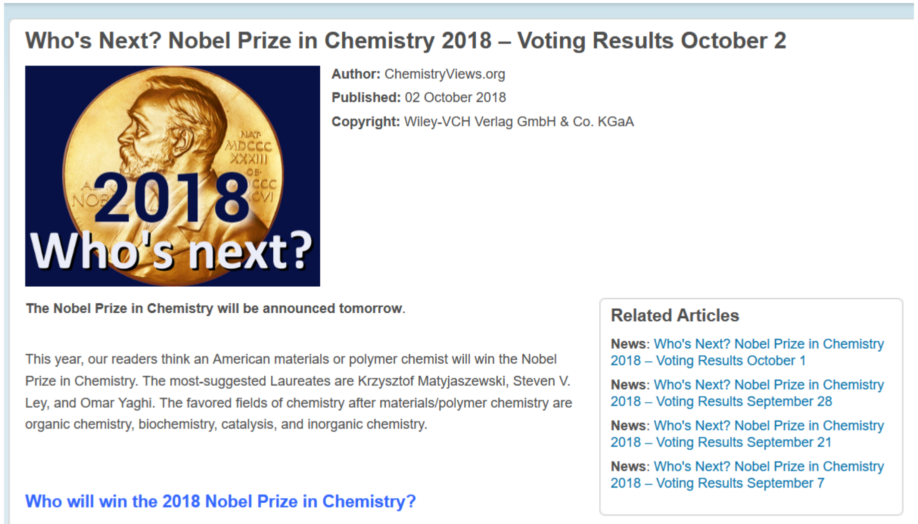


Figure 2. Correlation of experimental and theoretical (eq 1) molecular weights and polydispersities in bulk polymerization of styrene at 130 °C with $[1\text{-PECl}]_0/[CuCl]_0/[bpy]_0 = 1:1:3$.



Who's Next? Nobel Prize in Chemistry 2018 – Voting Results October 2

Author: ChemistryViews.org
Published: 02 October 2018
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The Nobel Prize in Chemistry will be announced tomorrow.

This year, our readers think an American materials or polymer chemist will win the Nobel Prize in Chemistry. The most-suggested Laureates are Krzysztof Matyjaszewski, Steven V. Ley, and Omar Yaghi. The favored fields of chemistry after materials/polymer chemistry are organic chemistry, biochemistry, catalysis, and inorganic chemistry.

Who will win the 2018 Nobel Prize in Chemistry?

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Who's Next? Nobel Prize in Chemistry 2019 – Voting Results September 20

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Published: 20 September 2019
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The Nobel Prize in Chemistry will be announced on October 9, 2019.

So far, our readers think a European materials or polymer chemist will win the 2019 Nobel Prize in Chemistry. The most suggested Laureates are Krzysztof Matyjaszewski, Ewine van Dishoeck, and Omar M. Yaghi.

Who do *you* think will be honored this year? Make your predictions here.

Who will win the 2019 Nobel Prize in Chemistry?

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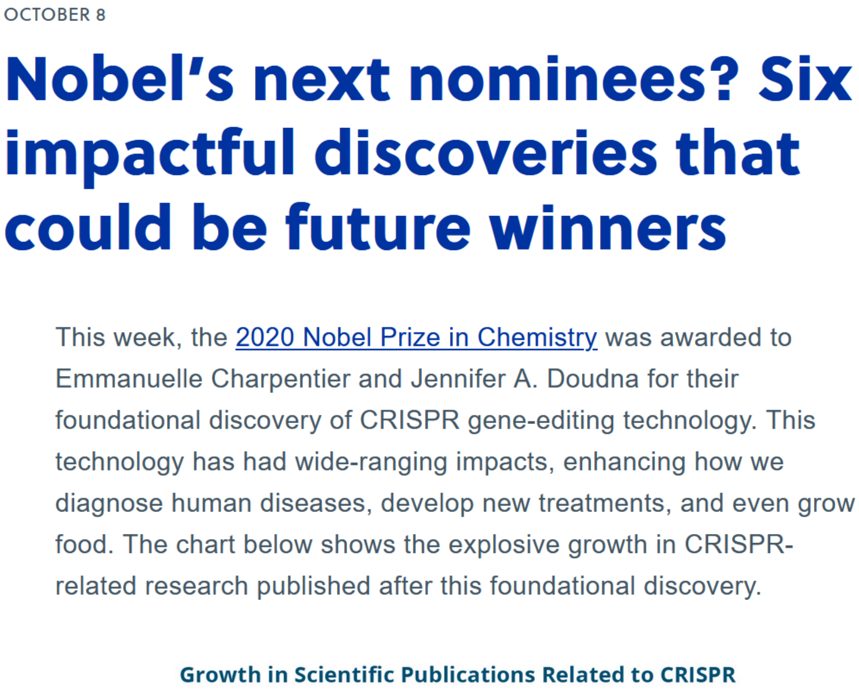
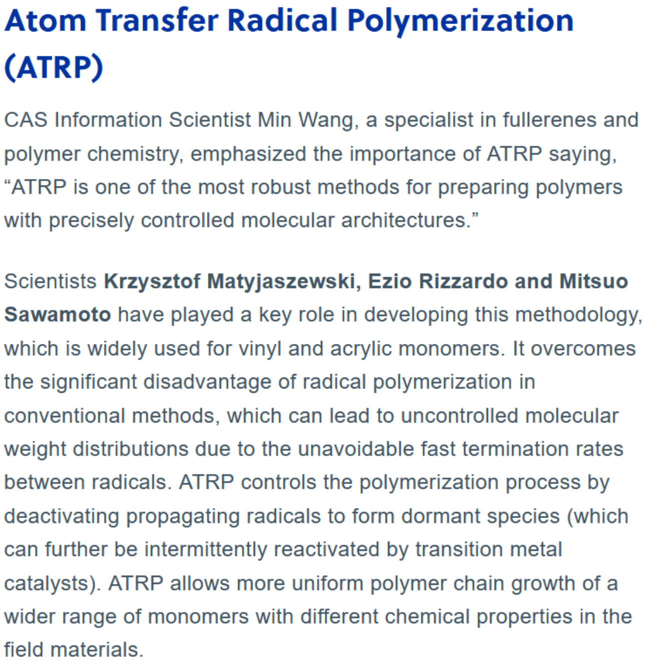


OCTOBER 8

Nobel's next nominees? Six impactful discoveries that could be future winners

This week, the 2020 Nobel Prize in Chemistry was awarded to Emmanuelle Charpentier and Jennifer A. Doudna for their foundational discovery of CRISPR gene-editing technology. This technology has had wide-ranging impacts, enhancing how we diagnose human diseases, develop new treatments, and even grow food. The chart below shows the explosive growth in CRISPR-related research published after this foundational discovery.

Growth in Scientific Publications Related to CRISPR

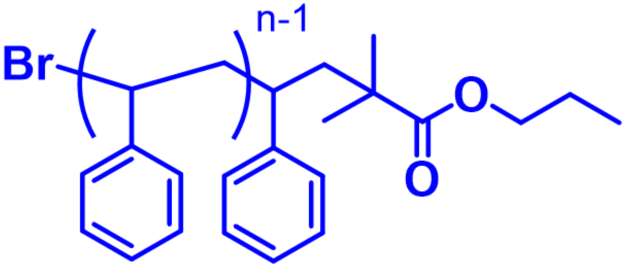


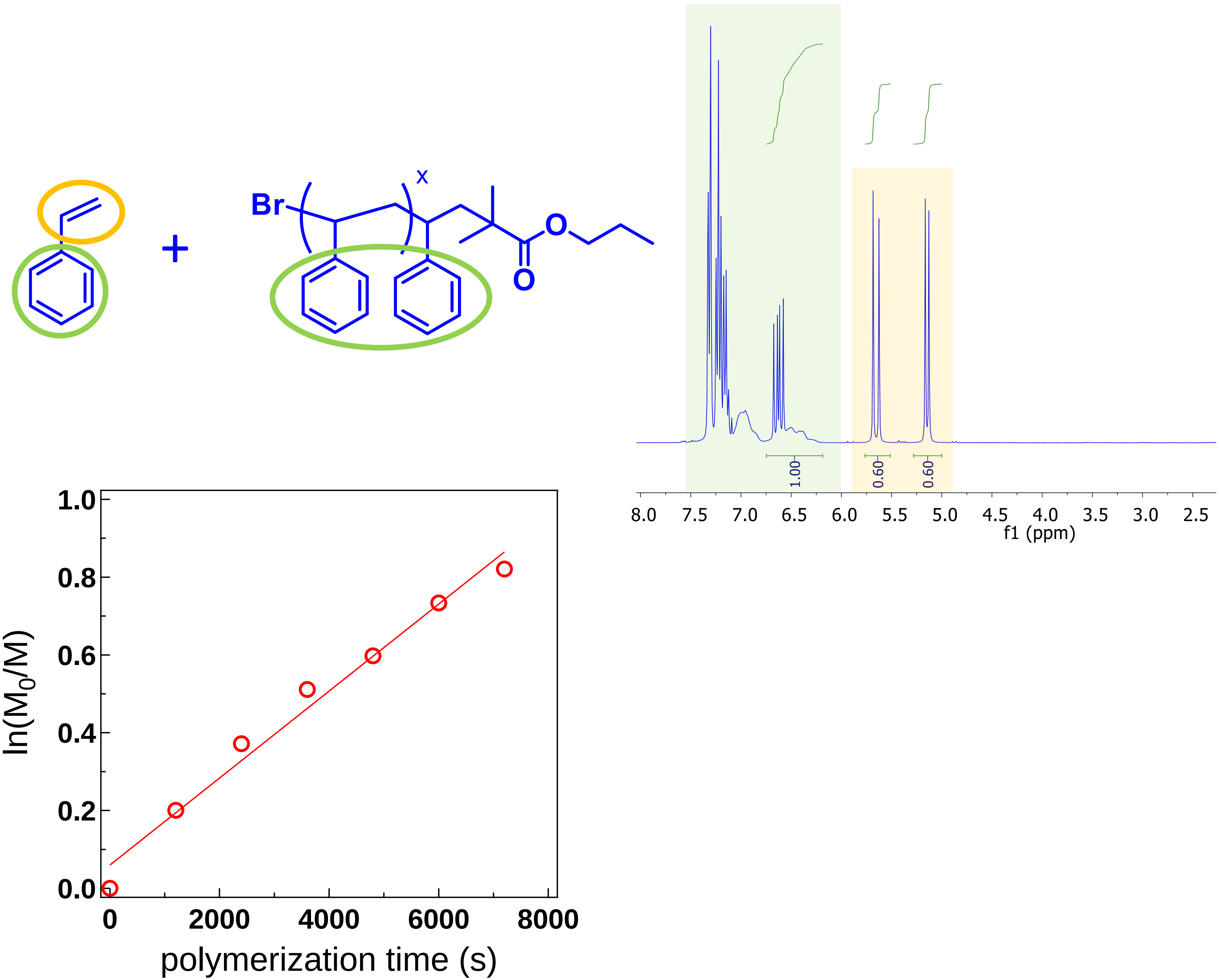
Atom Transfer Radical Polymerization (ATRP)

CAS Information Scientist Min Wang, a specialist in fullerenes and polymer chemistry, emphasized the importance of ATRP saying, "ATRP is one of the most robust methods for preparing polymers with precisely controlled molecular architectures."

Scientists **Krzysztof Matyjaszewski, Ezio Rizzardo and Mitsuo Sawamoto** have played a key role in developing this methodology, which is widely used for vinyl and acrylic monomers. It overcomes the significant disadvantage of radical polymerization in conventional methods, which can lead to uncontrolled molecular weight distributions due to the unavoidable fast termination rates between radicals. ATRP controls the polymerization process by deactivating propagating radicals to form dormant species (which can further be intermittently reactivated by transition metal catalysts). ATRP allows more uniform polymer chain growth of a wider range of monomers with different chemical properties in the field materials.

Synthesis of low-molar mass PS by heterogeneous ATRP

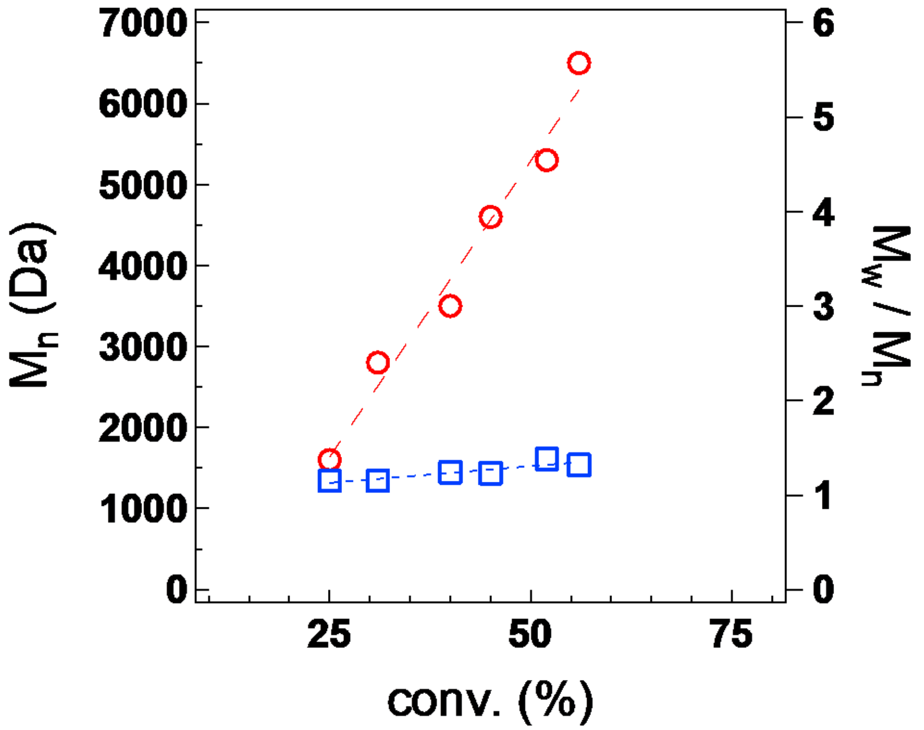


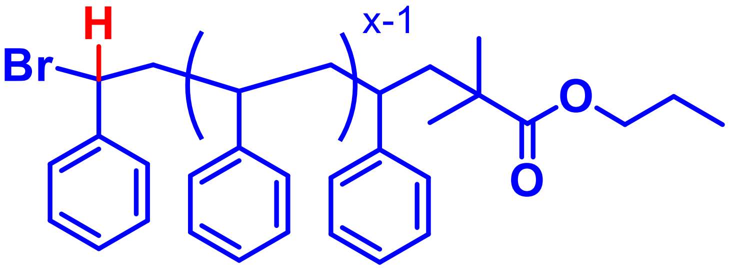

+
Br
x
O
O
1.00
0.60
0.60
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
ln(M0/M)
0
2000
4000
6000
8000
polymerization time (s)

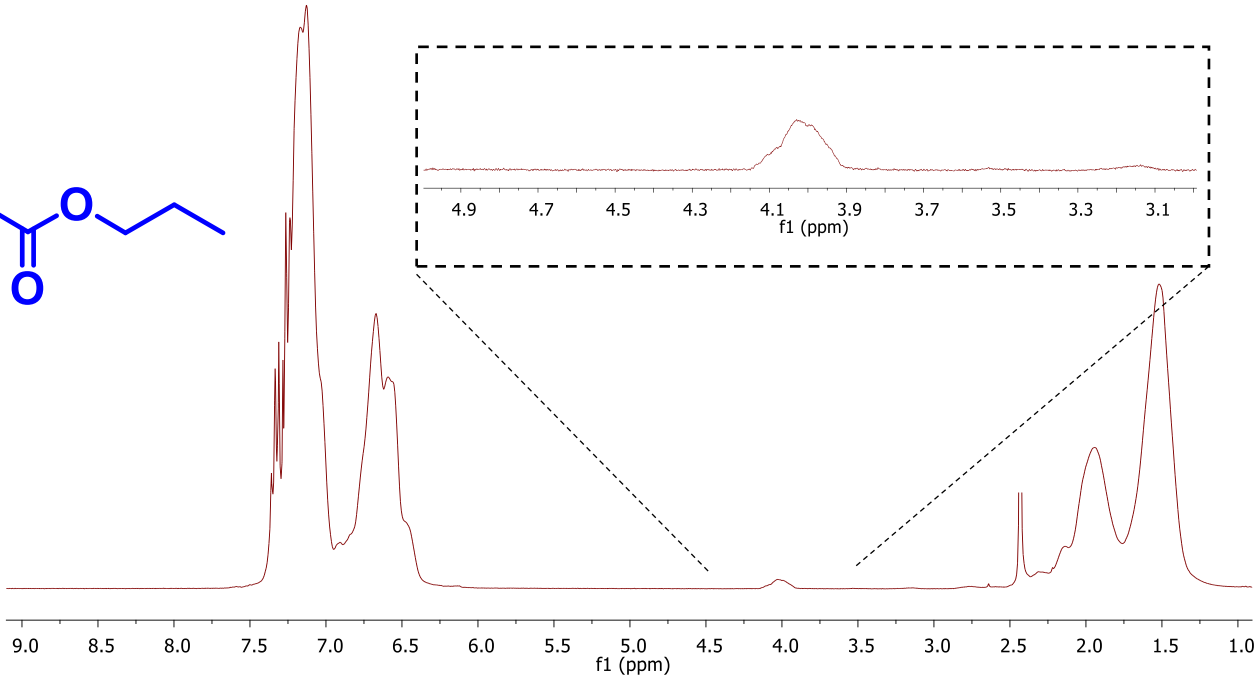
We stopped polymerization at 66% conversion

M_n(th.) = 6800 Da

M_n(exp.) = 6500 Da
PDI = 1.32







J. Am. Chem. Soc. **1997,** *119,* 674−680

Controlled/"Living" Radical Polymerization. Kinetics of the Homogeneous Atom Transfer Radical Polymerization of Styrene

Krzysztof Matyjaszewski,* Timothy E. Patten,[1] and Jianhui Xia

Contribution from the Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Received September 25, 1996®

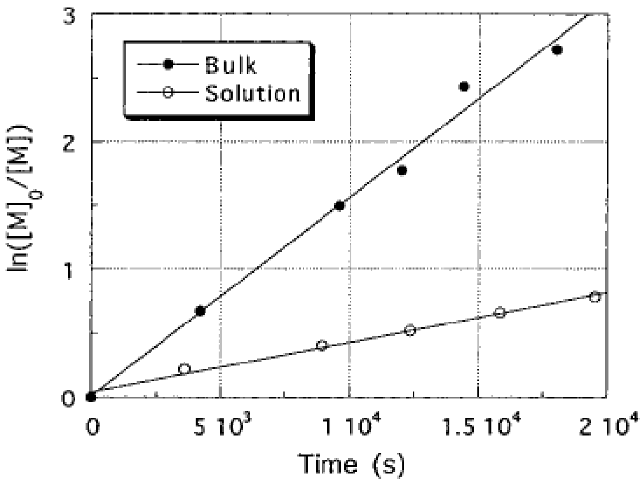


Figure 1. Semilogarithmic kinetic plots for the bulk and solution ATRPs of styrene at 110 °C. Bulk: $[\text{styrene}]_0 = 8.7$ M; $[\text{CuBr}]_0 = [\text{dNbipy}]_0/2 = 0.087$ M; $[\text{1-PEBr}]_0 = 0.087$ M. 50% (v/v) solution in diphenyl ether: $[\text{styrene}]_0 = 4.3$ M; $[\text{CuBr}]_0 = [\text{dNbipy}]_0/2 = 0.045$ M; $[\text{1-PEBr}]_0 = 0.045$ M. k_{app} (bulk) $= 1.6 \times 10^{-4}$ s^{-1}; k_{app} (solution) $= 3.9 \times 10^{-5}$ s^{-1}.

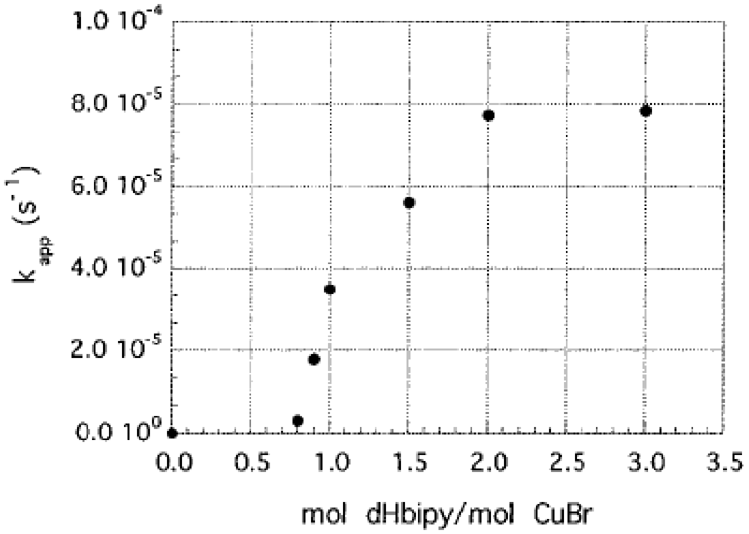


Figure 3. Plot of k_{app} as a function of increasing ligand concentration (dHbipy) at constant CuBr concentration for the bulk ATRP of styrene at 110 °C: $[\text{1-PEBr}]_0 = [\text{CuBr}]_0 = 0.087$ M.

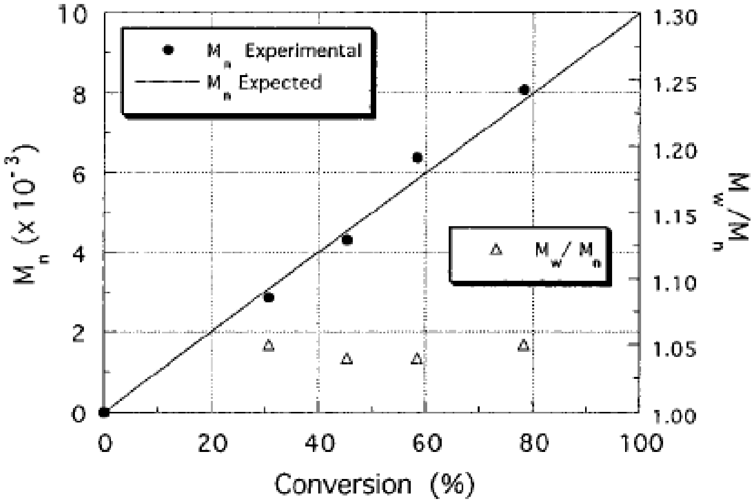


Figure 2. The dependence of molecular weight, M_n, and molecular weight distribution, M_w/M_n, upon monomer conversion for the bulk ATRP of styrene at 110 °C: $[\text{CuBr}]_0 = [\text{1-PEBr}]_0 = [\text{dNbipy}]_0/2 = 0.087$ M.

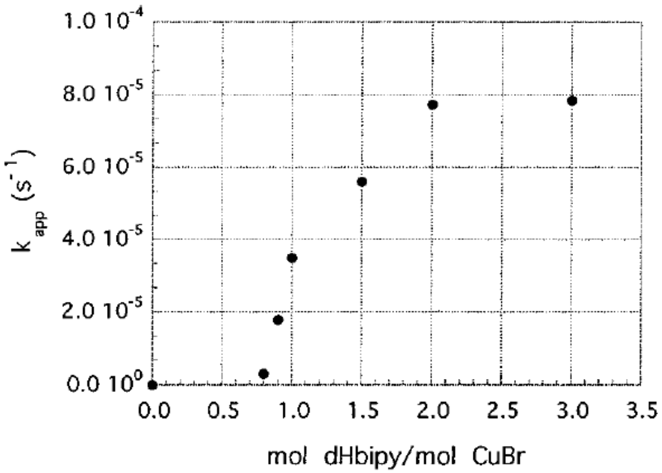


Figure 3. Plot of k_{app} as a function of increasing ligand concentration (dHbipy) at constant CuBr concentration for the bulk ATRP of styrene at 110 °C: $[\text{1-PEBr}]_0 = [\text{CuBr}]_0 = 0.087$ M.

$$K_{eq} = \frac{k_{act}}{k_{deact}} = \frac{[\text{P}^\bullet][\text{Cu(II)X}]}{[\text{Cu(I)}][\text{PX}]}$$

$$R_p = k_{app}[\text{M}] = k_p[\text{P}^\bullet][\text{M}] = k_p K_{eq}[\text{In}]\frac{[\text{Cu(I)}]}{[\text{Cu(II)X}]}[\text{M}]$$

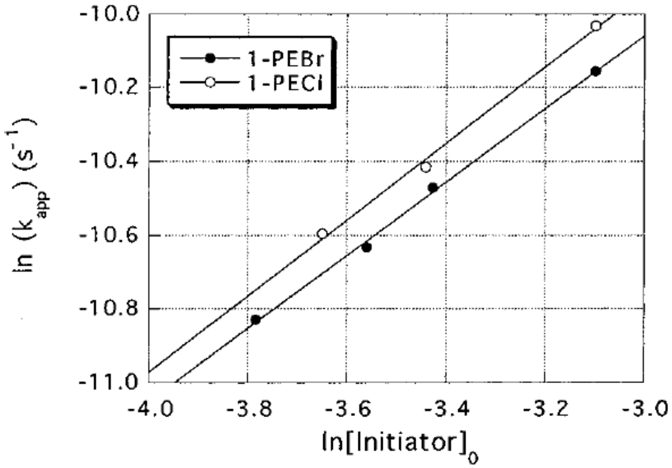


Figure 4. Reaction orders for the initiators, 1-PEBr (110 °C) and 1-PECl (130 °C), for the ATRP of styrene in diphenyl ether: $[\text{styrene}]_0 = 4.34$ M; $[\text{CuX}]_0 = [\text{dNbipy}]_0/2 = 0.045$ M. Slope (Br) = 0.99; Slope (Cl) = 1.04.

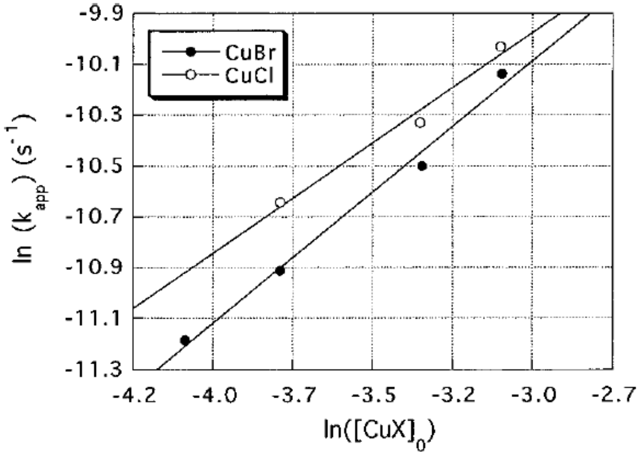
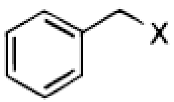
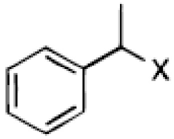


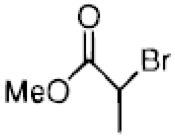
Figure 5. Reaction orders for CuBr (110 °C) and CuCl (130 °C) for the ATRP of styrene in diphenyl ether: $[\text{styrene}]_0 = 4.34$ M; $[\text{1-PEX}]_0 = 0.045$ M, $[\text{CuX}]_0 = [\text{dNbipy}]_0/2$. Slope (Cl) = 0.87; Slope (Br) = 1.03.



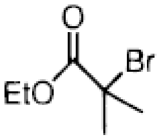
BzX



1-PEX



MeBrP



Et-2-BriB

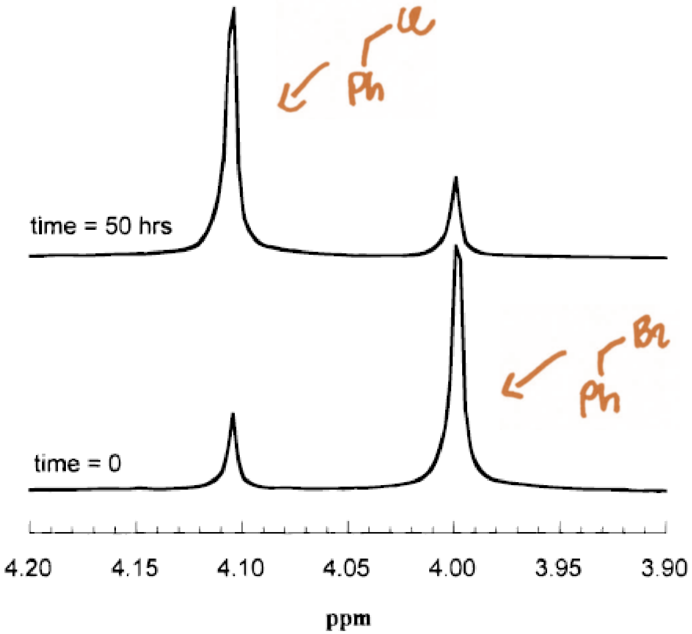


Figure 1. ^{1}H NMR spectra obtained from the model study of BzBr/CuCl at room temperature at the times indicated (last entry in Table 2). [BzBr] = 0.1 M, [CuCl] = 0.1 M, [dNbpy] = 0.2 M solvent = benzene-d_6.

Table 1. Percentage of R−Cl as a Function of Time in R−X/Cu−Y Halide Exchange Reactions As Monitored by Gas Chromatography (GC)[a]

	% R−Cl			
system (R−X/Cu−Y)	10 min	25 min	40 min	90 min
BzBr/CuCl[b]	66	78	81	
BzCl/CuBr[b]	94	90	87	82
1-PEBr/CuCl[b]	87	91	91	
1-PECl/CuBr[b]		90	88	89
Et-2-BriB/CuCl[c]	91	91	91	
MeBrP/CuCl[c]	79	84	85	

[a] [R−X] = 0.1 M, [Cu−Y] = 0.1 M, [dNbpy] = 0.2 M, [internal standard] = 0.05 M, solvent = benzene, temperature = 90 °C. [b] GC internal standard = chlorobenzene. [c] GC internal standard = dimethoxybenzene.

Table 2. Percentage of R−Cl as a Function of Time in R−X/Cu−Y Halide Exchange Reactions As Monitored by ^{1}H NMR Spectroscopy (Solvent = Benzene-d_6)

system (R−X/Cu−Y)	temp (°C)	reaction time	% R−Cl
BzBr/CuCl[a]	100	120 min	83
BzCl/CuBr[b]	100	120 min	82
1-PEBr/CuCl[c]	90	21 min	89
1-PECl/CuBr[c]	90	20 min	86
BzBr/CuCl[d]	room temp	50 h	83

[a] [BzBr] = 0.2 M, [CuCl] = 0.2 M, [dNbpy] = 0.4 M. [b] [BzCl] = 0.15 M, [CuCl] = 0.15 M, [dNbpy] = 0.3 M. [c] [1-PEX] = 0.1 M, [Cu−Y] = 0.1 M, [dNbpy] = 0.2 M. [d] [BzBr] = 0.1 M, [Cu−Cl] = 0.1 M, [dNbpy] = 0.2 M.

Synthesis of Acrylate and Methacrylate Block Copolymers Using Atom Transfer Radical Polymerization

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Received July 1, 1998; Revised Manuscript Received September 2, 1998

Table 1. Conditions for PMMA Macroinitiator and Acrylate−MMA Block Copolymer Syntheses Using PMMA as Macroinitiator at 90 °C[a]

expt no.	amt of monomer (mL)	amt of solvent (mL)	[initiator] (M)	[CuX] (M)	[ligand] (M)	time (h)	M_n	M_w/M_n
1[b]	MMA (25)	DPE (25)	0.0468	0.0468 (0.01404)	0.01404	18.5	12 100	1.12
2[c]	BA (1.2)	DPE (1.2)	0.0346	0.0346	0.0692	21	19 000	1.15

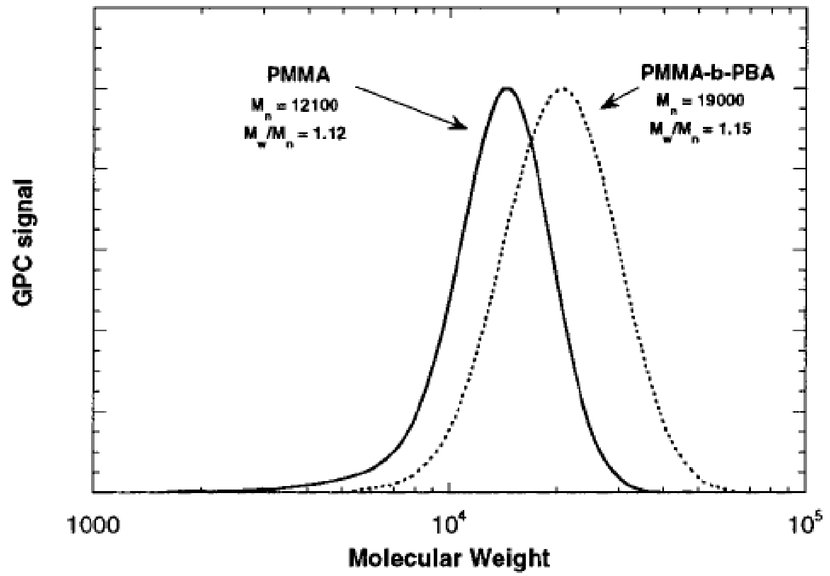


Figure 1. Molecular weight distributions of PMMA macroinitiator and PMMA-*b*-PBA diblock copolymer.

Table 1. Conditions for PMMA Macroinitiator and Acrylate−MMA Block Copolymer Syntheses Using PMMA as Macroinitiator at 90 °C[a]

expt no.	amt of monomer (mL)	amt of solvent (mL)	[initiator] (M)	[CuX] (M)	[ligand] (M)	time (h)	M_n	M_w/M_n
3[d]	MMA (2.0)	DPE (2.0)	0.0467	0.0234	0.0467	16	11 000	1.10
4[e]	MA (0.9)		0.0556	0.0556	0.111	20	20 500	1.15
5[f]	MMA (0.6)	DPE (0.6)	0.0167	0.0083[g]	0.0167	20	37 600	1.90

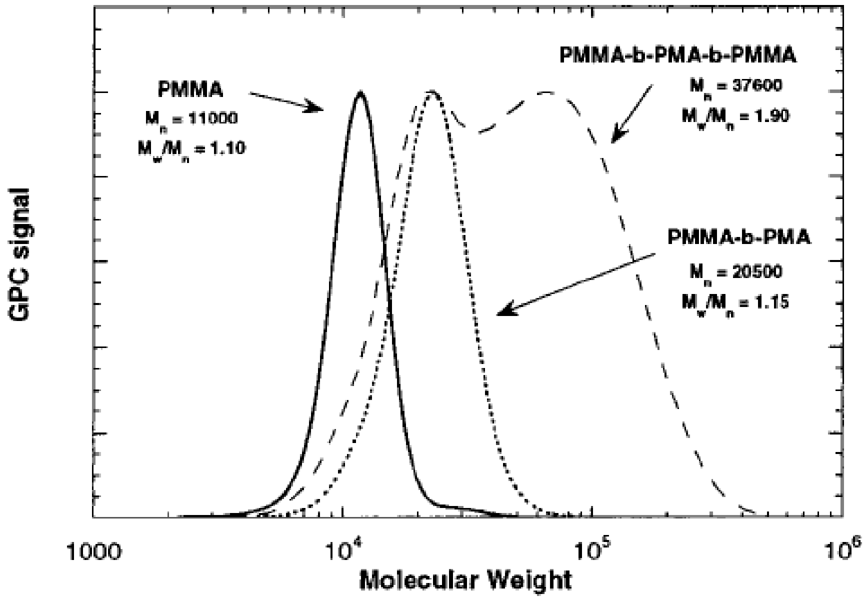


Figure 2. Molecular weight distributions of PMMA macroinitiator, PMMA-*b*-PMA diblock copolymer, and (attempted) PMMA-*b*-PMA-*b*-PMMA triblock copolymer.

Table 2. Conditions for PMA Macroinitiator and Acrylate−MMA Block Copolymer Synthesis Using PMA as Initiator[a]

expt no.	amt of monomer (mL)	amt of solvent (mL)	[initiator] (M)	[CuX] (M)	[ligand] (M)	temp (°C)	time (h)	M_n	M_w/M_n
6[b]	MA (10.0)		0.185	0.0925	0.0925	70	0.5	6 060	1.36
7[c]	MMA (5.0)	DPE (5.0)	0.0083	0.0166	0.0332	90	4.5	41 400	3.63

[a] DPE = diphenyl ether, EC = ethylene carbonate, B = benzene, MeXP = methyl 2-haloproprionate (halogen (X) = Cl or Br), PMDETA = *N,N,N′,N′,N″*-pentamethyldiethylenetriamine. [b] Initiator = MeClP, CuX = CuCl, L = PMDETA. [c] Initiator = PMA-Cl (expt 6), CuX = CuCl, L = dAbpy. [d] Initiator = MeBrP, CuX = CuBr, L = bpy. [e] Initiator = PMA (expt 8), CuX = CuCl, L = dNbpy. [f] Initiator = **1**, CuX = CuBr, L = dAbpy. [g] Initiator = PBA-Br (expt 10), CuX = CuCl, L = dAbpy.

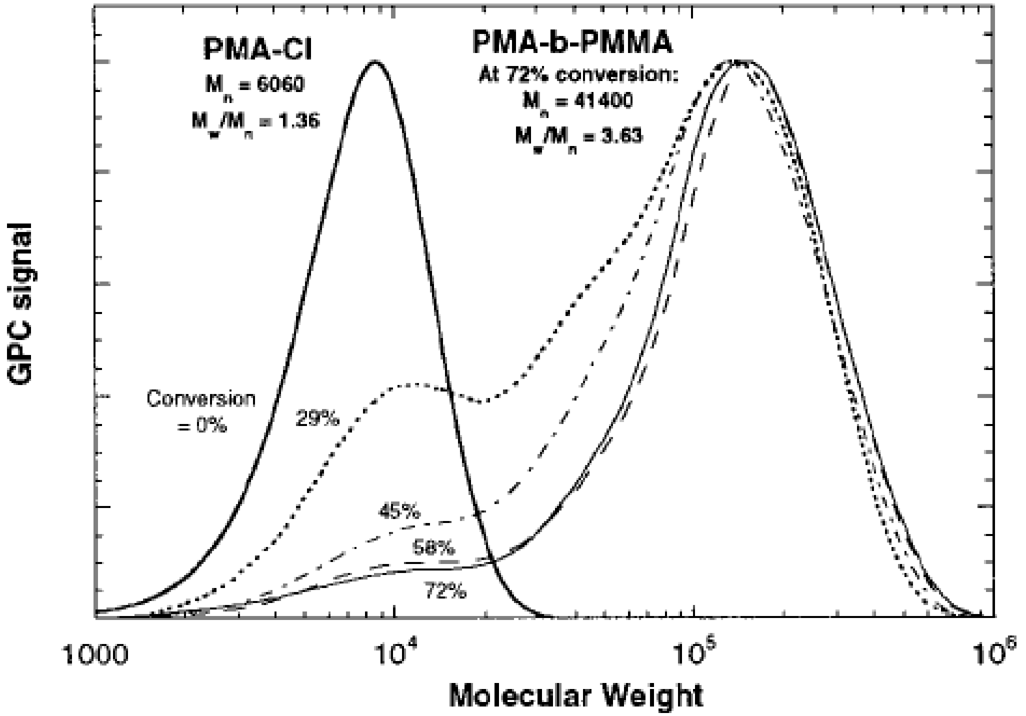


Figure 3. Molecular weight distributions of PMA-Cl macroinitiator and PMA-*b*-PMMA diblock copolymer at various monomer conversions (indicated in the figure).

Table 2. Conditions for PMA Macroinitiator and Acrylate−MMA Block Copolymer Synthesis Using PMA as Initiator[a]

expt no.	amt of monomer (mL)	amt of solvent (mL)	[initiator] (M)	[CuX] (M)	[ligand] (M)	temp (°C)	time (h)	M_n	M_w/M_n
8[d]	MA (5.0)	EC (5.0)	0.111	0.0555	0.333	90	1.5	5 910	1.32
9[e]	MMA (5.0)	DPE (5.0)	0.0086	0.0172	0.0339	90	18	63 900	1.15

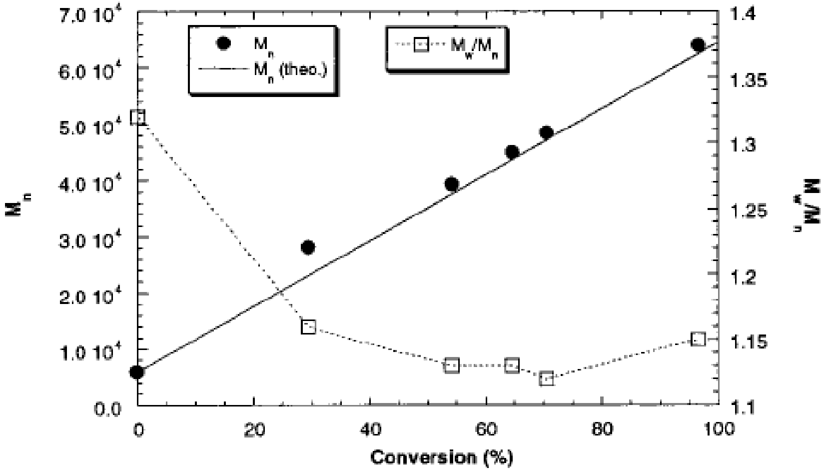
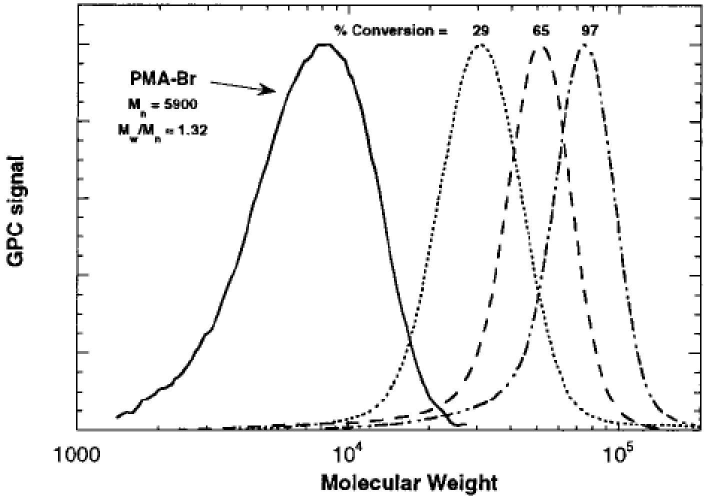


Figure 5. Molecular weight and polydispersity evolution as a function of conversion for of the ATRP of MMA using PMA-Br as the initiator and CuCl/dNbpy as the catalyst.



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10[f]	BA (10.0)		0.01175	0.00816	0.0242	70	16	11 200	1.41
11[g]	MMA (1.0)	B (1.3)	0.0202	0.0409	0.0880	70	16	37 200	1.20

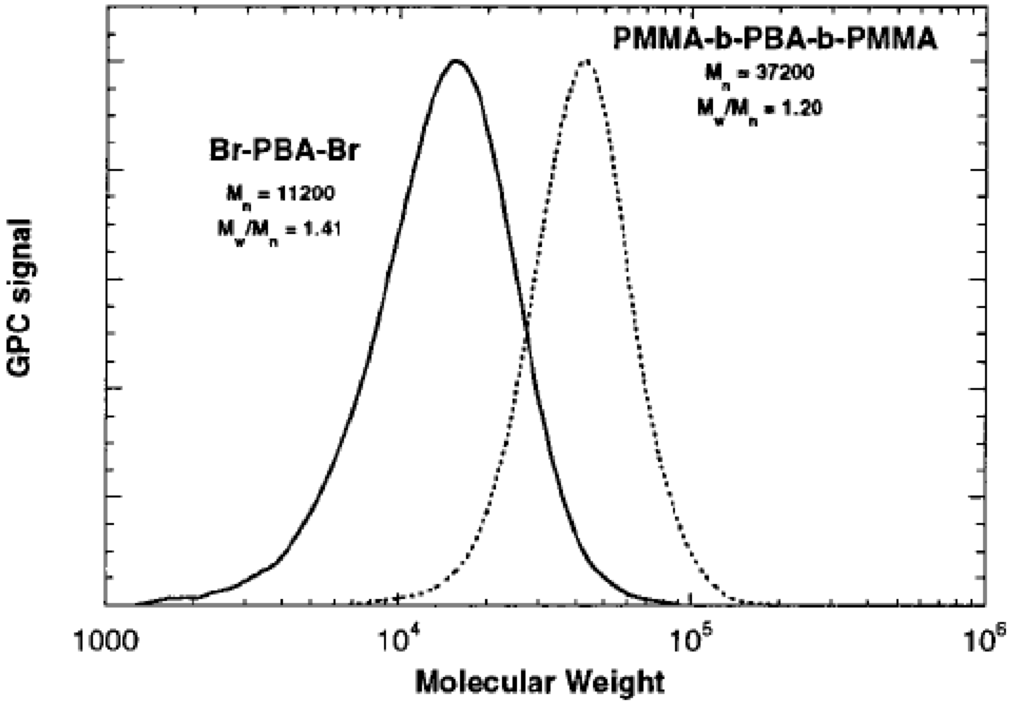
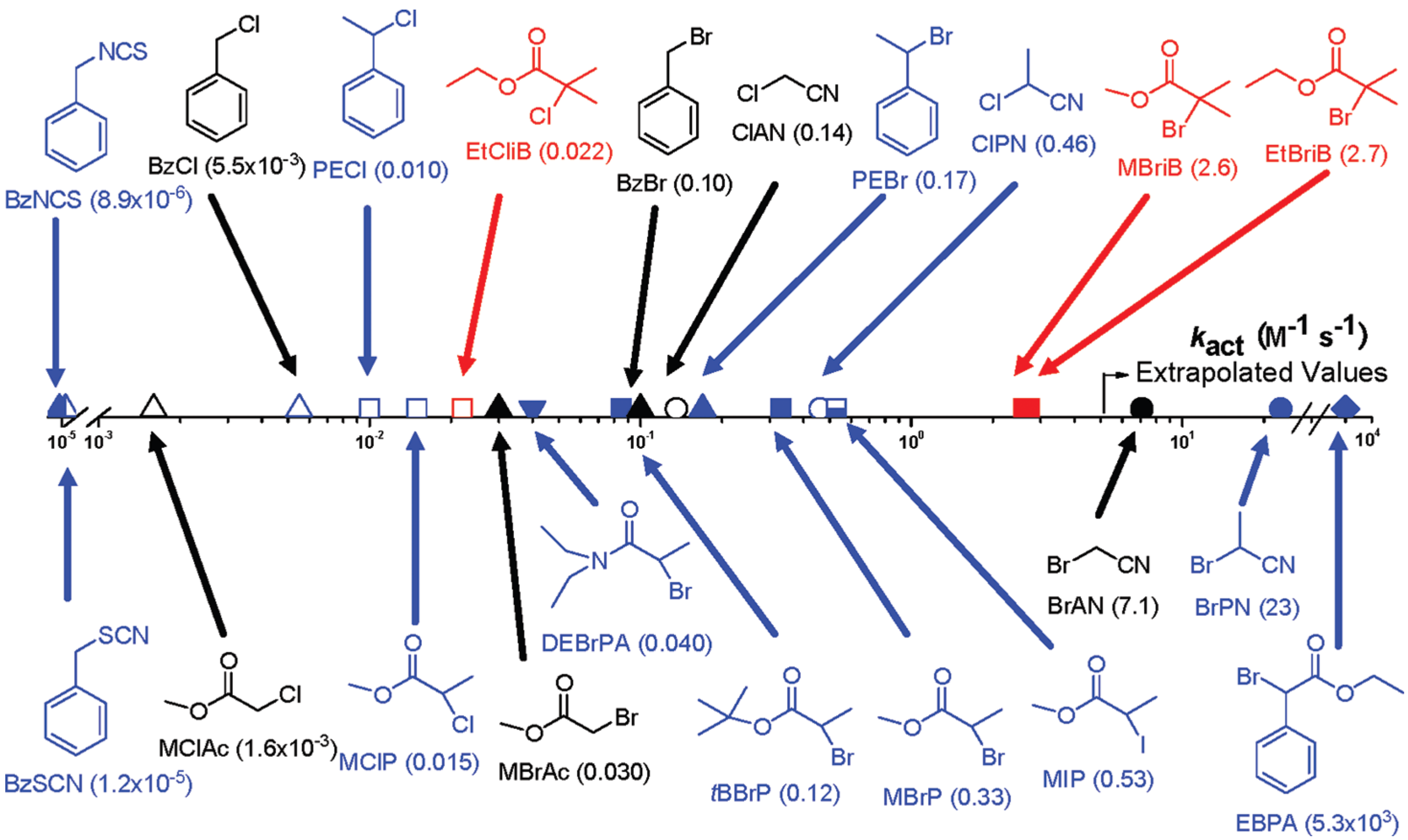


Figure 7. Molecular weight distributions of Br-PMA-Br macroinitiator and PMMA-*b*-PMA-*b*-PMMA triblock copolymer.

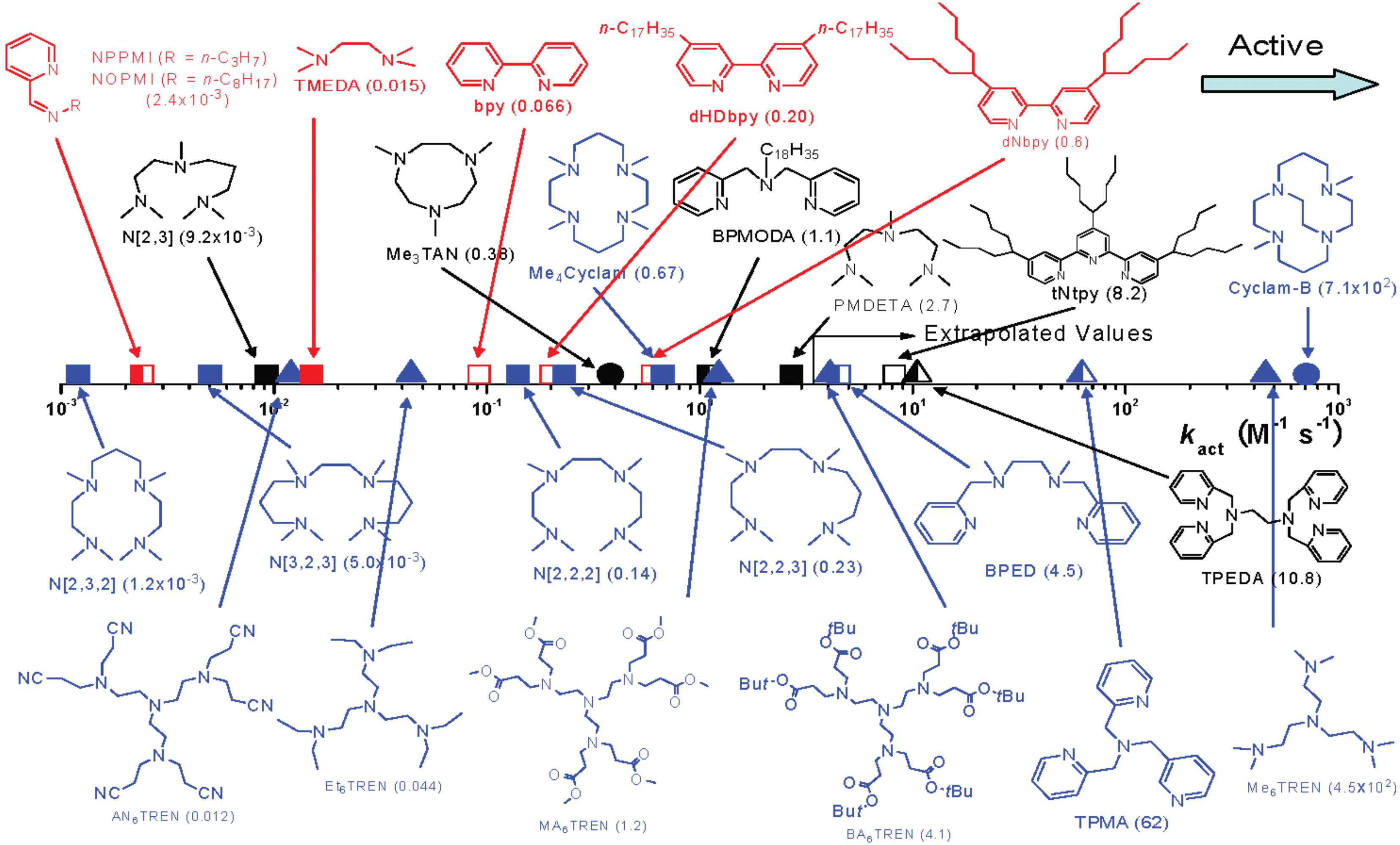
Effect of initiator on K_{act}



Tang, Matyjaszewski ; Macromolecules **2007**, 40, 1858–1863

Matyjaszewski ; *Macromolecules* **2012**, 45, 4015−4039

Effect of ligand on K_{act}



K. Matyjaszewski *Macromolecules* **2012**, 45, 4015−4039

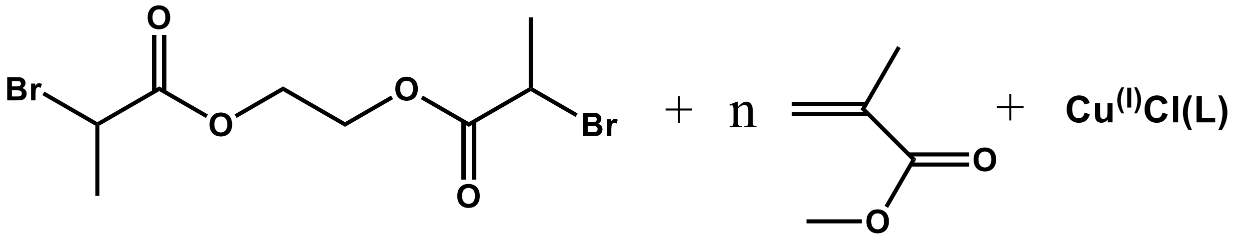
Per favore completa il generico equilibrio ATRP di attivazione/deattivazione riportato sotto nel caso di un iniziatore alogenuro alchilico R-X, e un complesso di Cu con formula generica $\mathrm{Cu^{+1}X/L_2}$:

$$\mathrm{R\text{-}X} \;+\; \mathrm{Cu^{+1}X/L_2} \quad \underset{k_d}{\overset{k_a}{\rightleftarrows}}$$

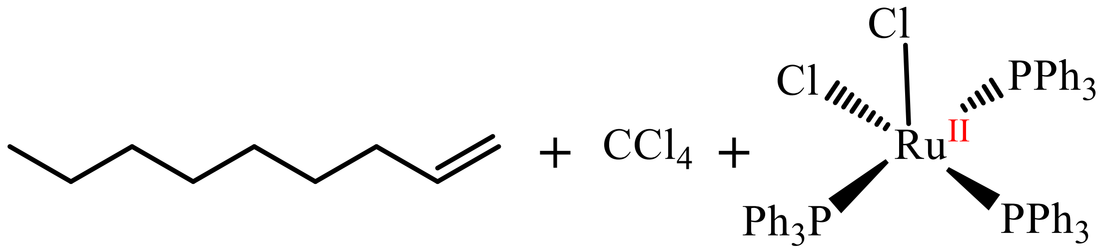
Per favore deriva dall'equilibrio riportato sopra l'espressione della costante di equilibrio (K_{eq}) per ATRP:

$$K_{eq} =$$

Per favore indica il prodotto della ATRP del *metil metacrilato* utilizzando i reagenti indicati sotto (si consideri **L** come legante generico).

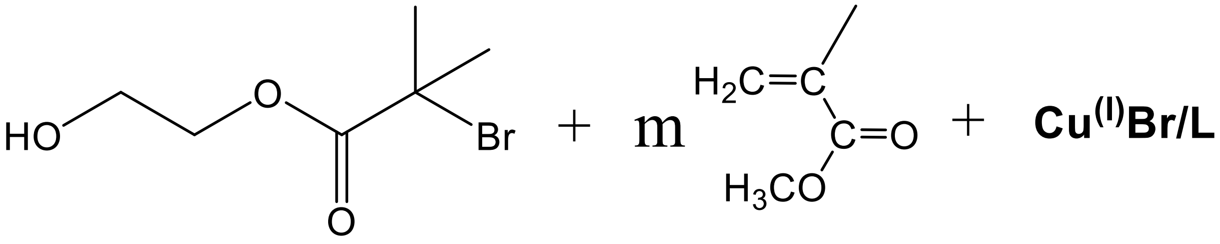


Si prega di esplicitare il composto organico maggioritario che si ottiene come prodotto dalla reazione di addizione di ***tetracloruro di carbonio*** a ***1-nonene*** catalizzata da ***diclorotris(trifenilfosfina)rutenio(II)***. Si prega inoltre di riportare i singoli passaggi coinvolti nella reazione.



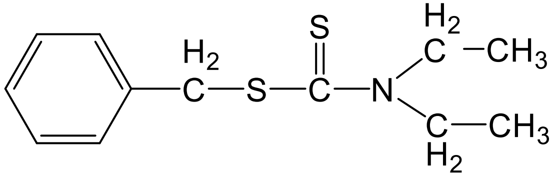
Si prega di riportare tramite opportuna formula chimica il prodotto (polimero) della reazione di polimerizzazione ATRP del *metil metacrilato* utilizzando i reagenti indicati di seguito. Si prega di esplicitare la natura chimica dei gruppi terminali del prodotto.

Si intenda che la polimerizzazione vada a completezza (conversione 100%) e che si utilizzi un generico legante "L" per generare il complesso di Cu.

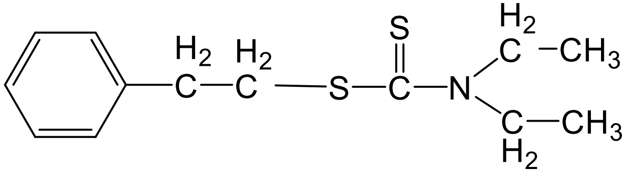


Topic: Iniferter-mediated controlled radical polymerization
Please provide the radical products originating from the UV-induced dissociation of compound (A) and (B) as discussed during the course.

(A)

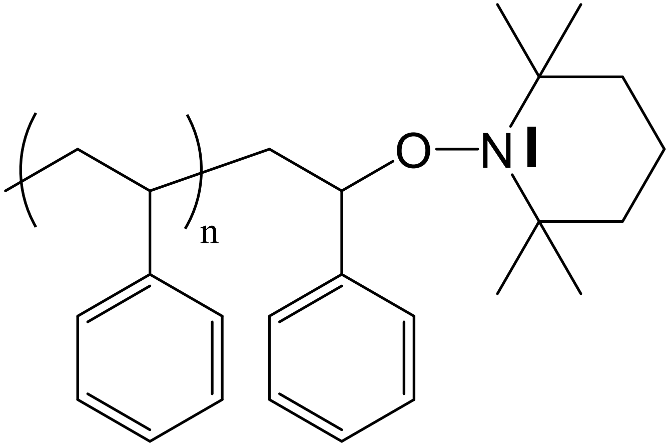


(B)



Topic: Nitroxide-mediated controlled radical polymerization

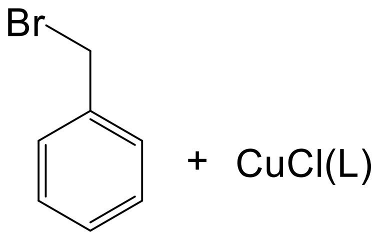
The presence of additives such as anhydrides and “activated” carboxylic acids during NMP allowed the polymerization to be performed at relatively low temperatures and relatively short reaction times. Please draw the molecular mechanism through which acetic anhydride interacts with the alkoxyamine function reported below during the polymerization.



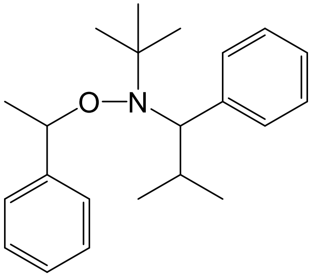
Topic: ATRP

Please report the general equilibrium reaction for the ATRP process which involves a metal complex $Cu^{I}Br(L)$ (where L denotes the organic ligand coordinated to the Cu^{I} center) and a propagating chain R_n-Br (or macroinitiator) in the presence of a generic monomer denoted as M

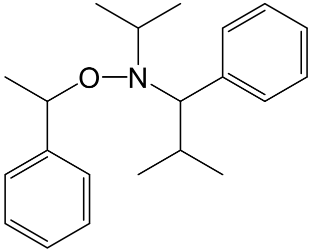
Please provide the species that can be isolated as major products from the reaction between the two compounds below.



Which one among the following alkoxyamine species produces the more stable nitroxide radical upon heating up the polymerization solution? Please justify your answer.



(A)



(B)