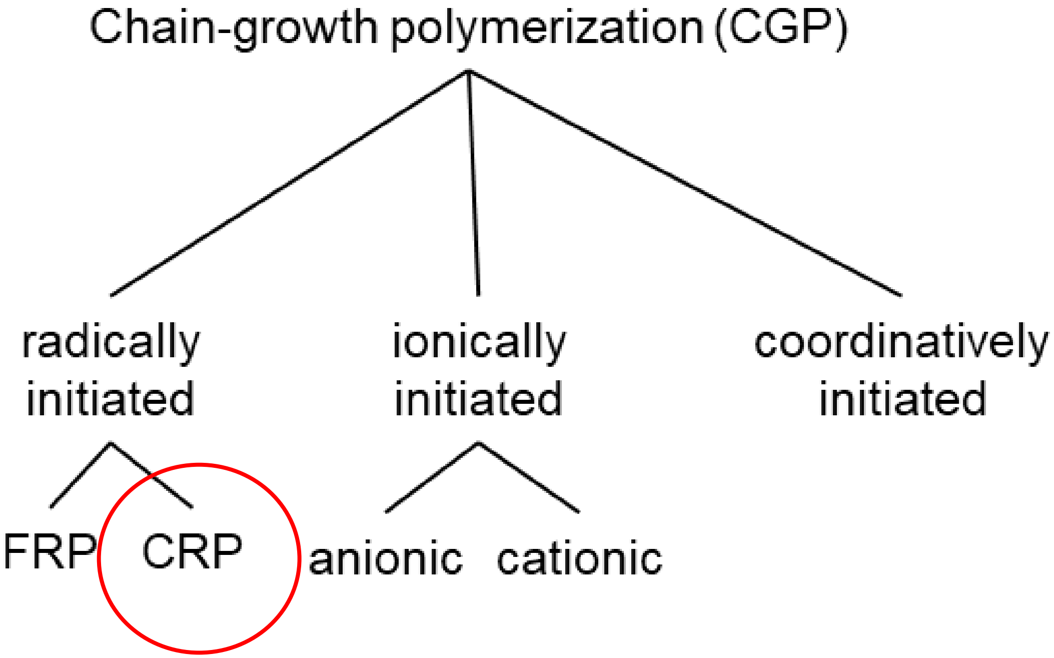
Polimerizzazioni a Catena
(chain-growth polymerizations)



Chain-growth polymerization (CGP)

radically initiated

ionically initiated

coordinatively initiated

FRP

CRP

anionic

cationic

Controlled Radical Polymerizations

OUTLINE

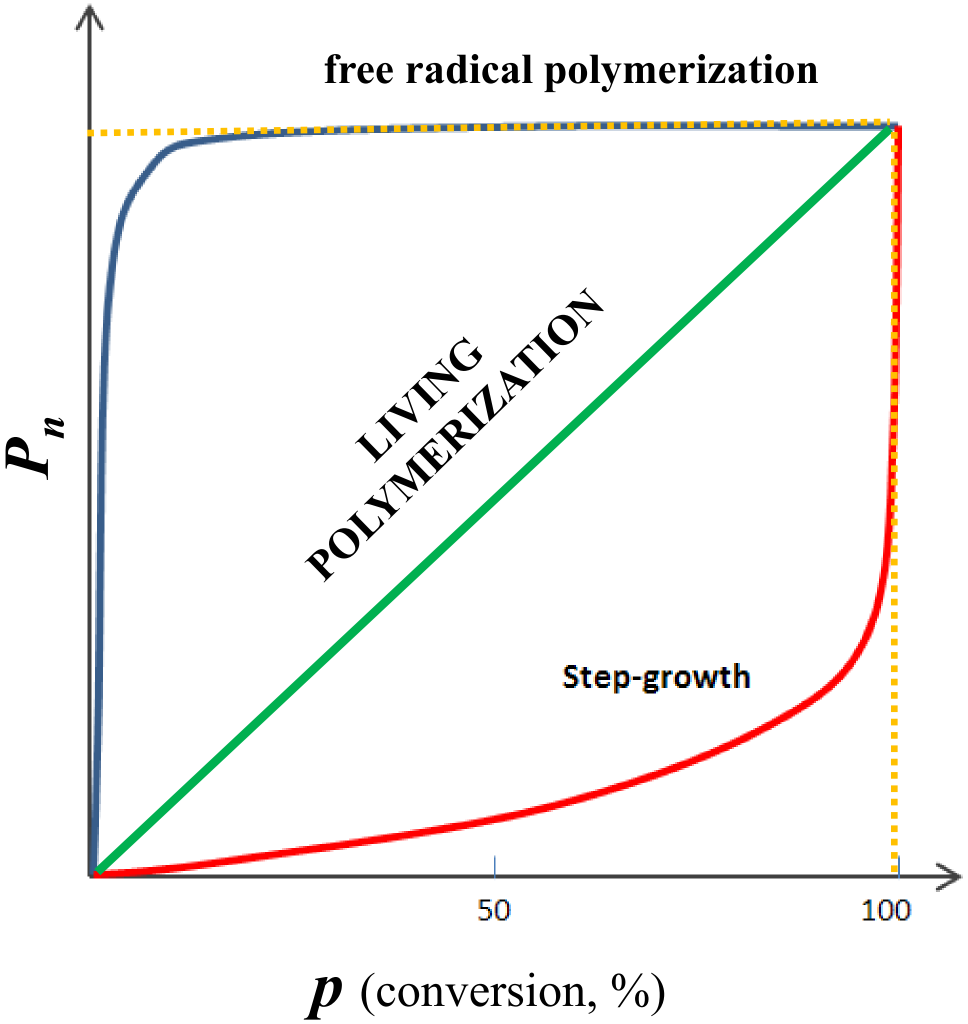
4. Controlled Radical Polymerization

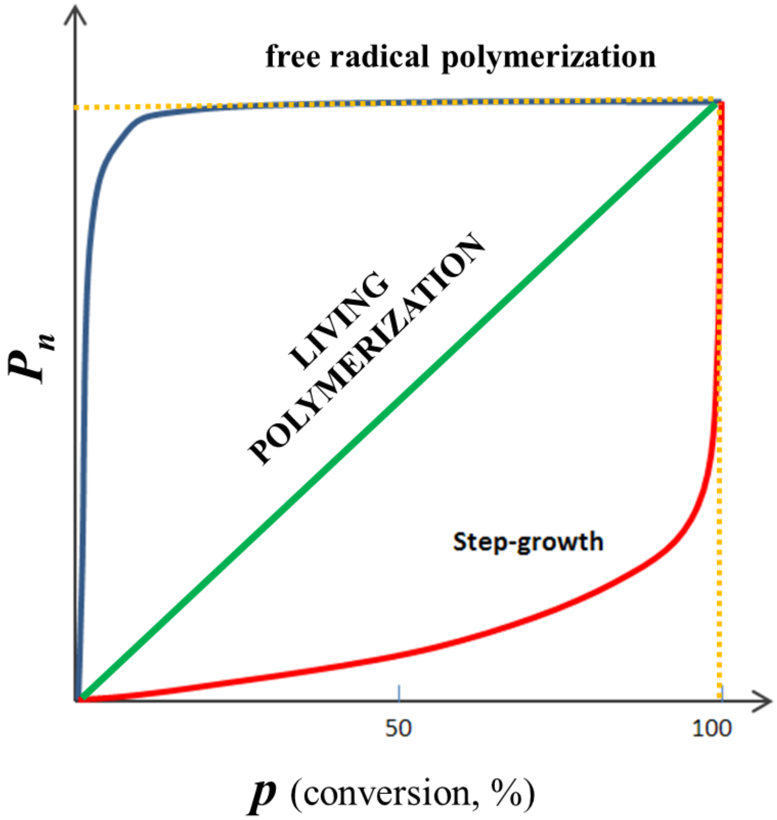
- The persistent radical Effect;
- Persistent or “stable” radicals: an historical overview
- **Initiator Transfer Terminator Agents** (*iniferter*)

- **Nitroxide-Mediated Polymerization (NMP)**
    - *free radical initiators in the presence of **TEMPO***
    - *from bimolecular initiators to **alkoxyamines***
    - *additives for NMP*
    - *development of alkoxyamines*

- **Transition metal complex-catalyzed CRP:**
    - *Radical addition of halide-substituted alkanes to olefins*
    - *The birth of **Atom Transfer Radical Polymerization** (ATRP)*
    - *mechanism of ATRP*
    - *homogeneous systems of ATRP*
    - *Halide exchange to improve control*
    - *block copolymerization*

Controlled Radical Polymerization (CRP)





Vi sono diversi **importanti criteri** per classificare una polimerizzazione come *vivente* o *living*:

- La velocità di iniziazione è significativamente piu' alta di quella di propagazione
- Reazioni di terminazione e trasferimento sono assenti
- In queste condizioni:

$$P_n = \frac{[M]_0}{[I]_0} \times p$$

<u>Questo risultato si ottiene se un numero costante di catene si mantiene durante la polimerizzazione.</u>

Iniziazione veloce: tutte le catene propagano prima che la reazione finisca

Assenza di trasferimento: il numero totale di catene non aumenta

Hans Fischer (UZH)

The Persistent Radical Effect in Controlled Radical Polymerizations

$$R_n - Y \underset{k_c}{\overset{k_d}{\rightleftarrows}} R_n^{\bullet} + Y^{\bullet}$$

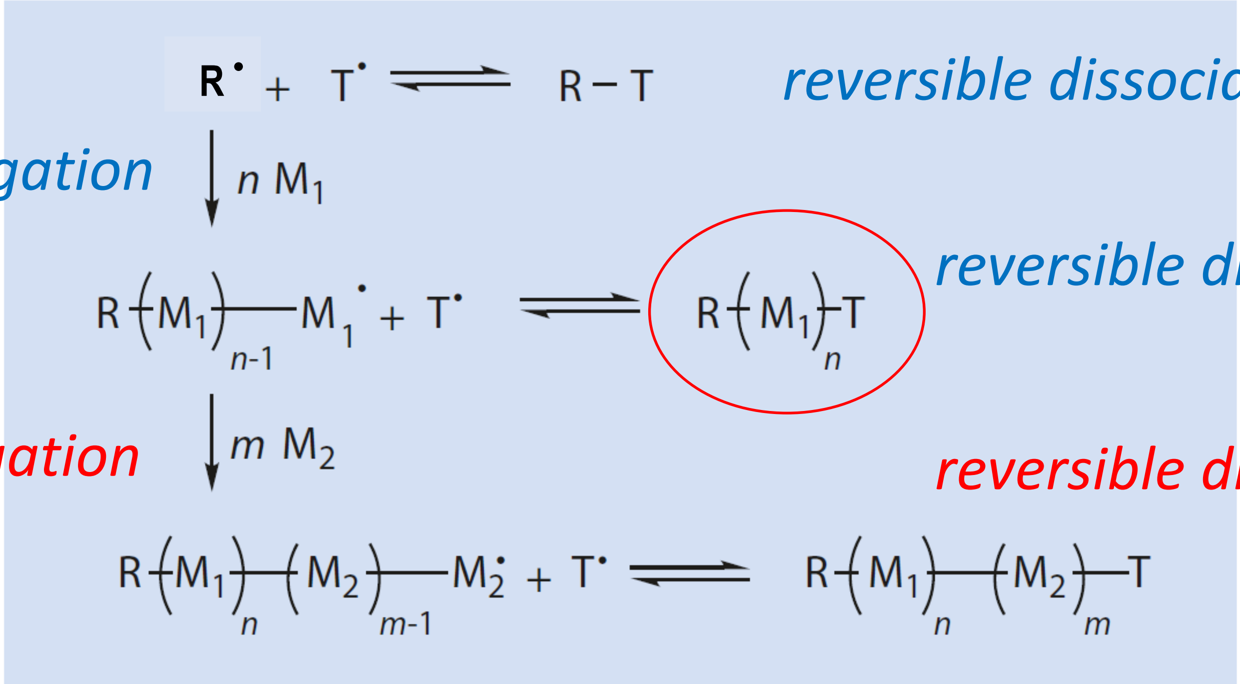
(1) *reversible dissociation*

$$R_n^{\bullet} + R_m^{\bullet} \xrightarrow{k_t} \text{products}$$

(2) *termination*

$$R_n^{\bullet} + M \xrightarrow{k_p} R_{n+1}^{\bullet}$$

(3) *propagation*



reversible dissociation

propagation

reversible dissociation

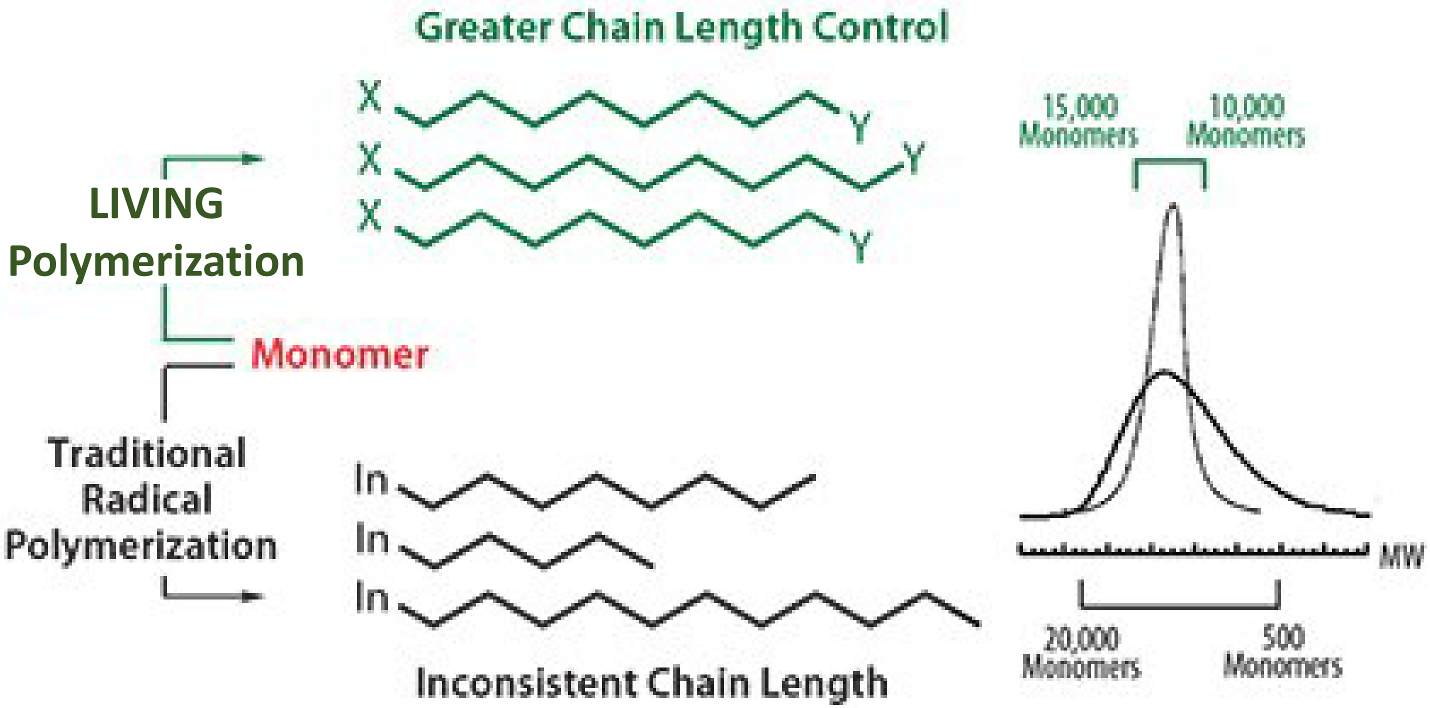
propagation

reversible dissociation

CRITERIA FOR LIVINGNESS

- **La velocità di iniziazione è significativamente piu' alta di quella di propagazione**
- **Reazioni di terminazione e trasferimento sono assenti**
- **In queste condizioni** $P_n = \frac{[M]_0}{[I]_0} x\, p$

- **Controllo dei gruppi terminali**
- **Facile sintesi di copolimeri a blocchi!**



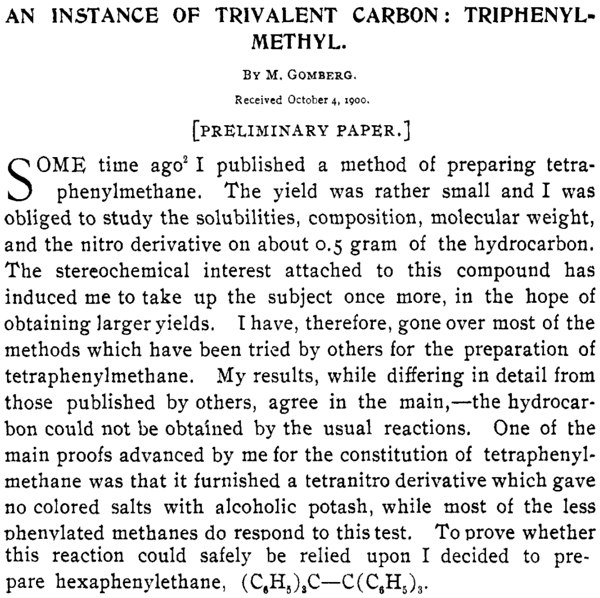
CRITERIA FOR LIVINGNESS

- **La velocità di iniziazione è significativamente piu’ alta di quella di propagazione**
- **Reazioni di terminazione e trasferimento sono assenti**
- **In queste condizioni** $P_n = \frac{[M]_0}{[I]_0} x\, p$

- **Controllo dei gruppi terminali**
- **Facile sintesi di copoloimeri a blocchi!**
- **Distribuzione di pesi molecolare stretta ($Đ \leq 1.3$)**

Prof. Moses Gomberg

University of Michigan, ***1900***



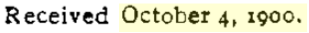
AN INSTANCE OF TRIVALENT CARBON: TRIPHENYLMETHYL.

BY M. GOMBERG.

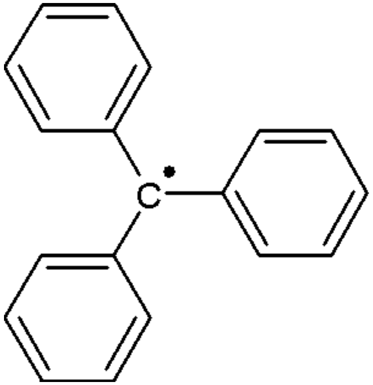
Received October 4, 1900.

[PRELIMINARY PAPER.]

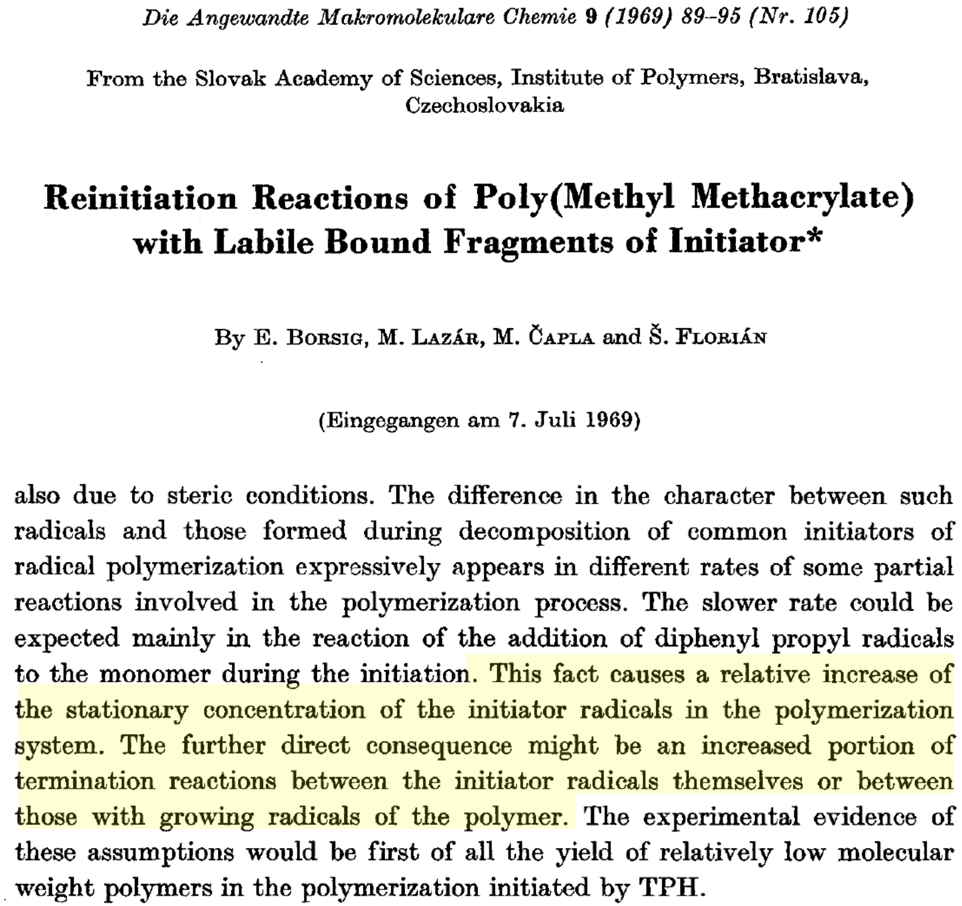
SOME time ago[2] I published a method of preparing tetraphenylmethane. The yield was rather small and I was obliged to study the solubilities, composition, molecular weight, and the nitro derivative on about 0.5 gram of the hydrocarbon. The stereochemical interest attached to this compound has induced me to take up the subject once more, in the hope of obtaining larger yields. I have, therefore, gone over most of the methods which have been tried by others for the preparation of tetraphenylmethane. My results, while differing in detail from those published by others, agree in the main,—the hydrocarbon could not be obtained by the usual reactions. One of the main proofs advanced by me for the constitution of tetraphenylmethane was that it furnished a tetranitro derivative which gave no colored salts with alcoholic potash, while most of the less phenylated methanes do respond to this test. To prove whether this reaction could safely be relied upon I decided to prepare hexaphenylethane, $(C_6H_5)_3C—C(C_6H_5)_3$.



Received October 4, 1900.



<u>First example of persistent radical?</u>



Die Angewandte Makromolekulare Chemie **9** *(1969) 89–95 (Nr. 105)*

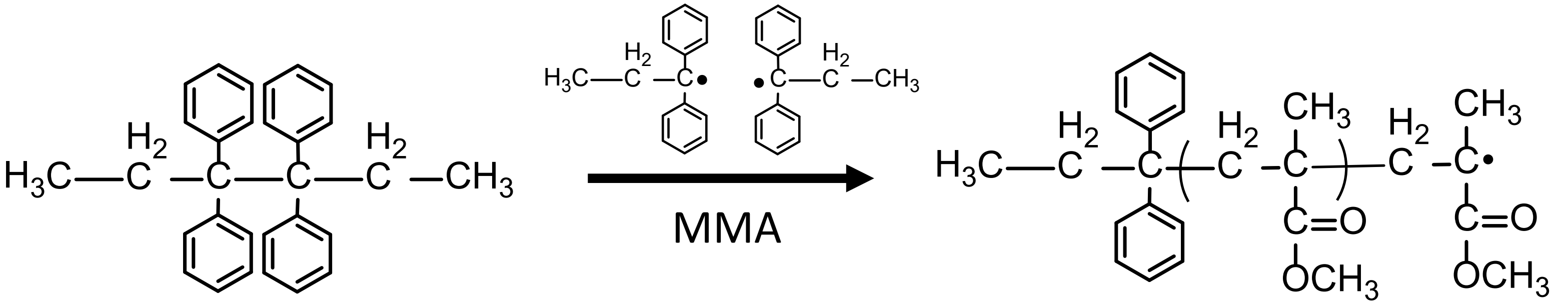
From the Slovak Academy of Sciences, Institute of Polymers, Bratislava,
Czechoslovakia

Reinitiation Reactions of Poly(Methyl Methacrylate) with Labile Bound Fragments of Initiator*

By E. Borsig, M. Lazár, M. Čapla and Š. Florián

(Eingegangen am 7. Juli 1969)

also due to steric conditions. The difference in the character between such radicals and those formed during decomposition of common initiators of radical polymerization expressively appears in different rates of some partial reactions involved in the polymerization process. The slower rate could be expected mainly in the reaction of the addition of diphenyl propyl radicals to the monomer during the initiation. This fact causes a relative increase of the stationary concentration of the initiator radicals in the polymerization system. The further direct consequence might be an increased portion of termination reactions between the initiator radicals themselves or between those with growing radicals of the polymer. The experimental evidence of these assumptions would be first of all the yield of relatively low molecular weight polymers in the polymerization initiated by TPH.



This was something in between a persistent radical and a common FRP initiator

“Interrupted” polymerization

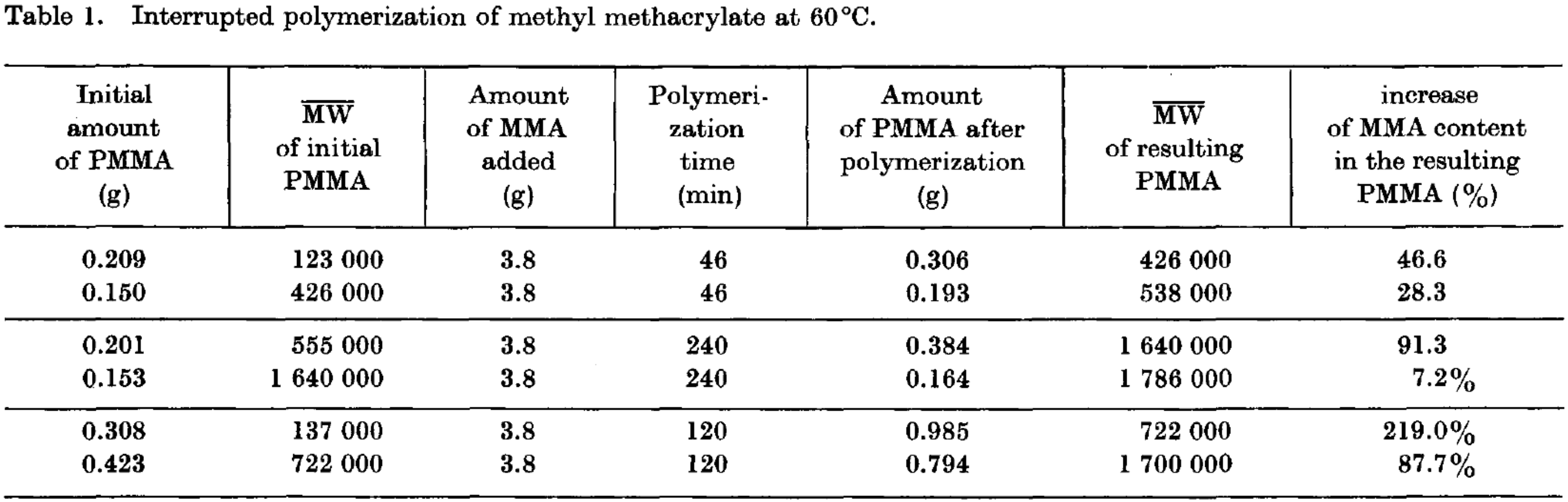


Table 1. Interrupted polymerization of methyl methacrylate at 60 °C.

Initial amount of PMMA (g)	$\overline{\text{MW}}$ of initial PMMA	Amount of MMA added (g)	Polymerization time (min)	Amount of PMMA after polymerization (g)	$\overline{\text{MW}}$ of resulting PMMA	increase of MMA content in the resulting PMMA (%)
0.209	123 000	3.8	46	0.306	426 000	46.6
0.150	426 000	3.8	46	0.193	538 000	28.3
0.201	555 000	3.8	240	0.384	1 640 000	91.3
0.153	1 640 000	3.8	240	0.164	1 786 000	7.2%
0.308	137 000	3.8	120	0.985	722 000	219.0%
0.423	722 000	3.8	120	0.794	1 700 000	87.7%

INItiator transFER TERminator agents

The first example of CRP

Prof. Takayuki Otsu
Osaka University

*A Review: Otsu, J. Polym. Sci. A 38, 2121 (**2000**)*

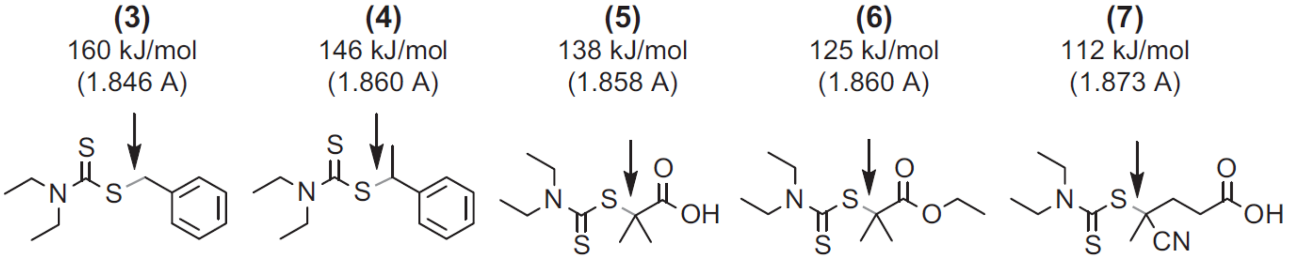
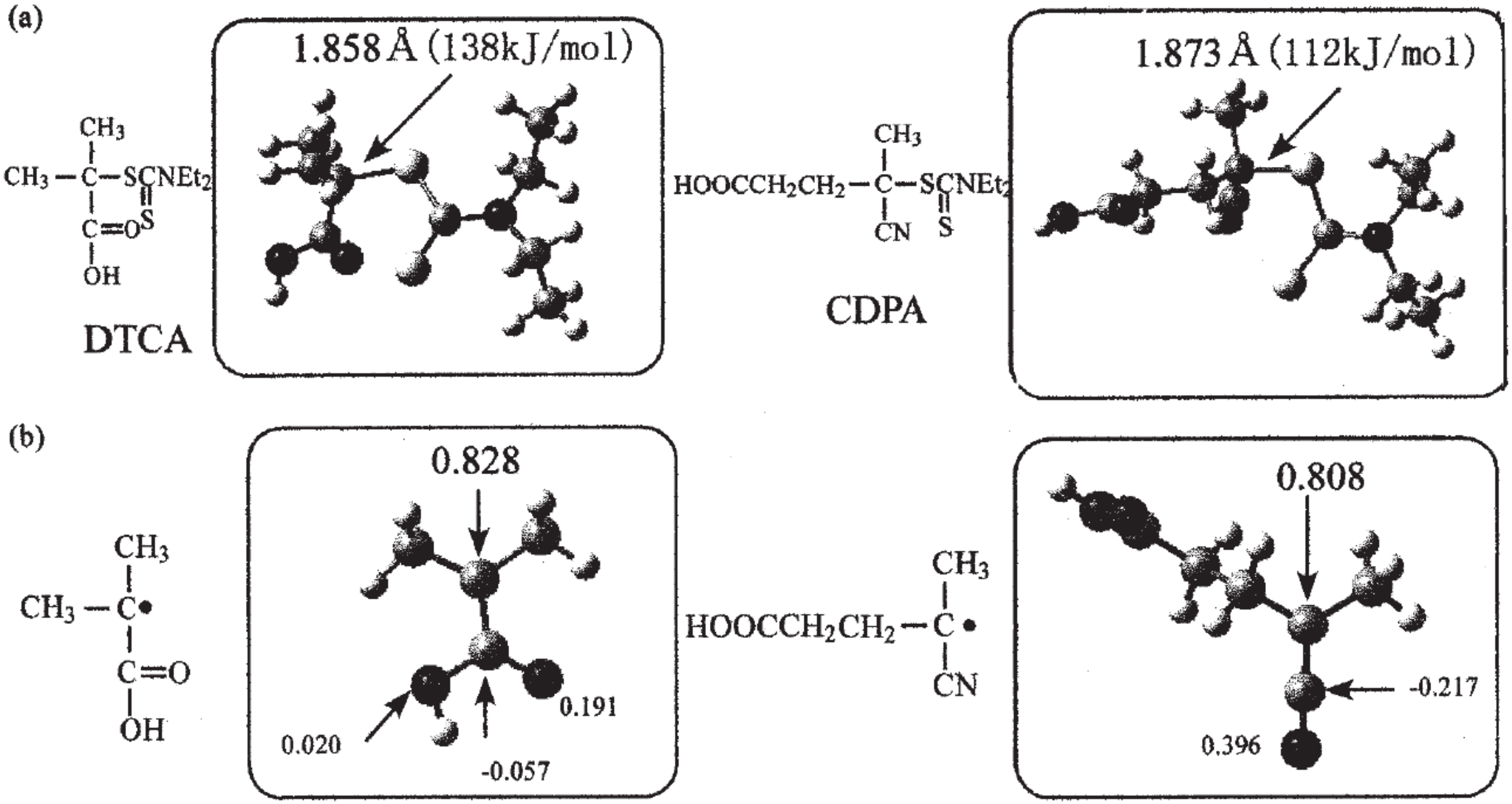
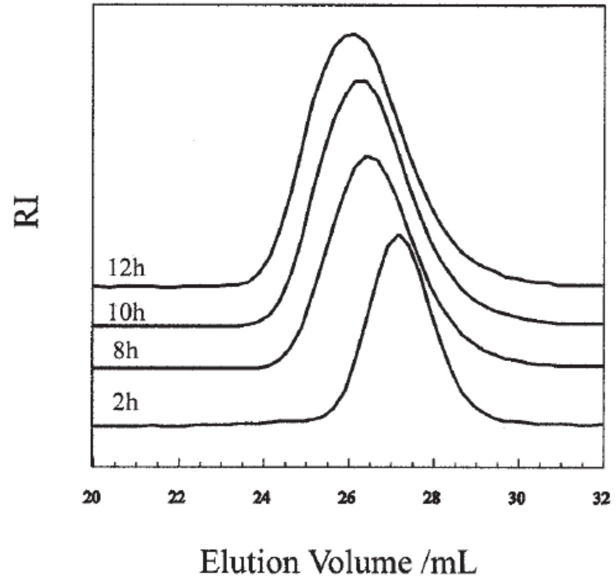


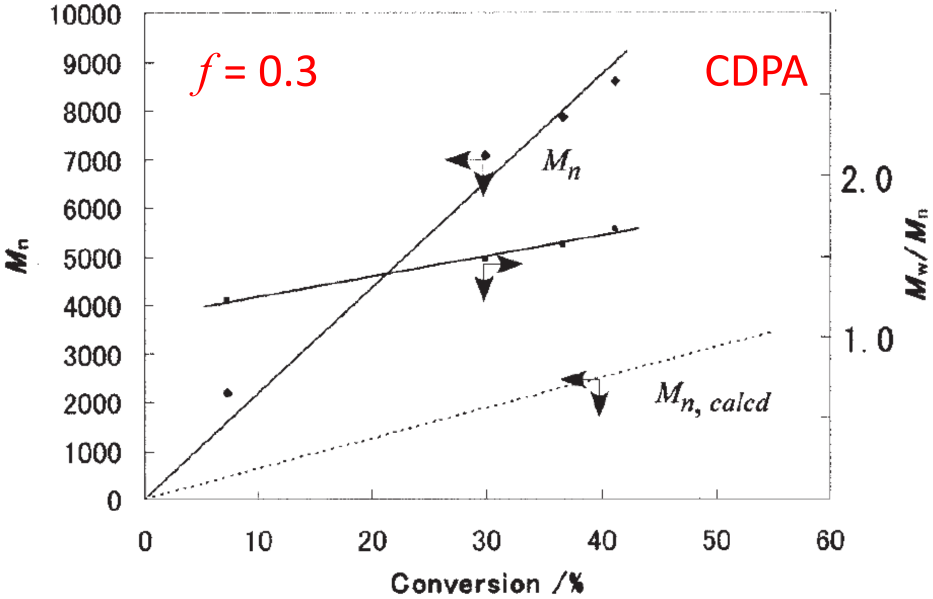
Chart 3.2 Several model compounds and their C–S bond lengths and dissociation energies.

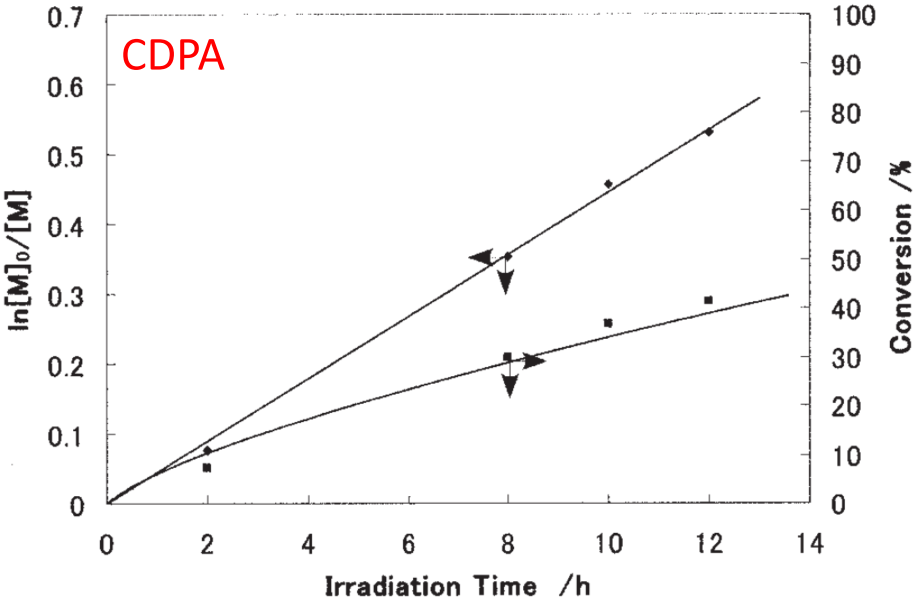


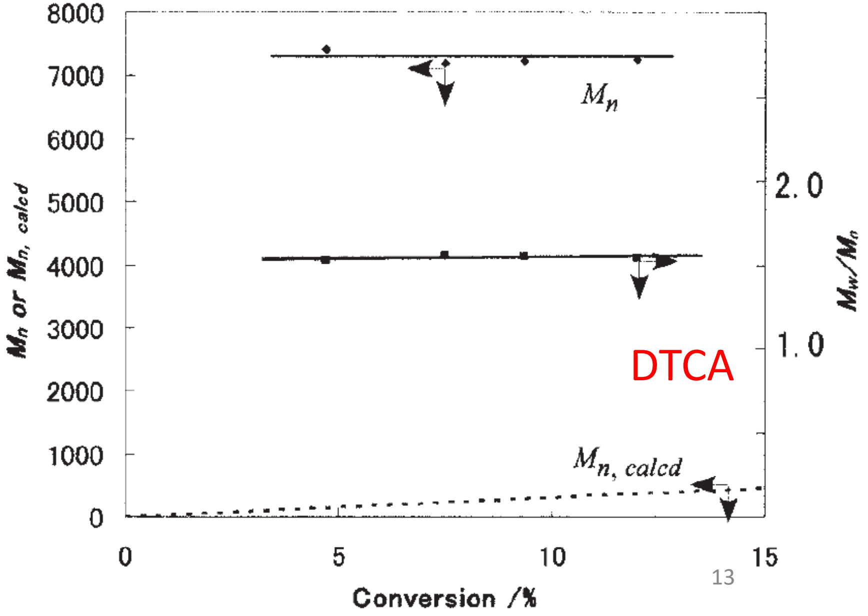
*Ishizu et al. J. Appl. Polym. Sci. 95, 413 (**2005**)*

Polymerization of Styrene in benzene by INIFERTER: CDPA vs DTCA

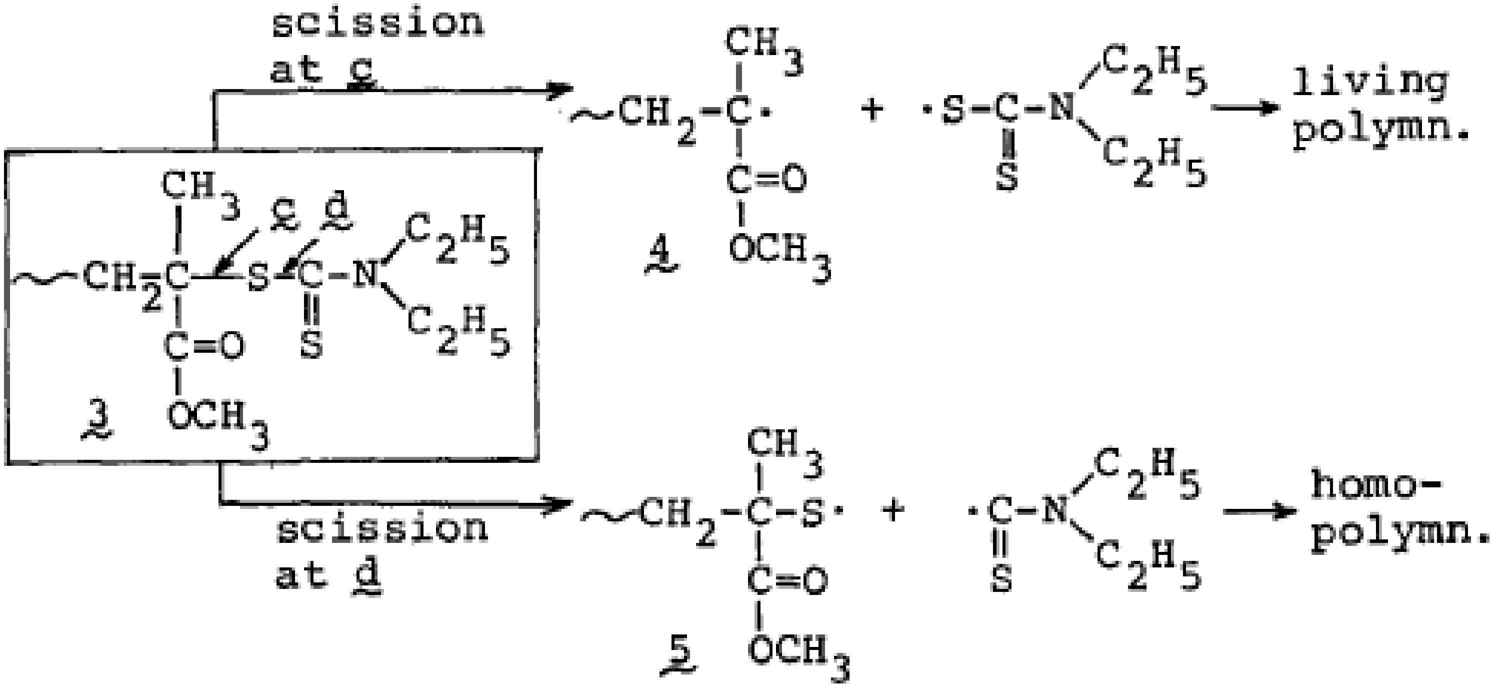








*Ishizu et al. J. Appl. Polym. Sci. 95, 413 (**2005**)*



(9)

(10)

Polymerization of methacrylic acid in methanol by INIFERTER: CDPA

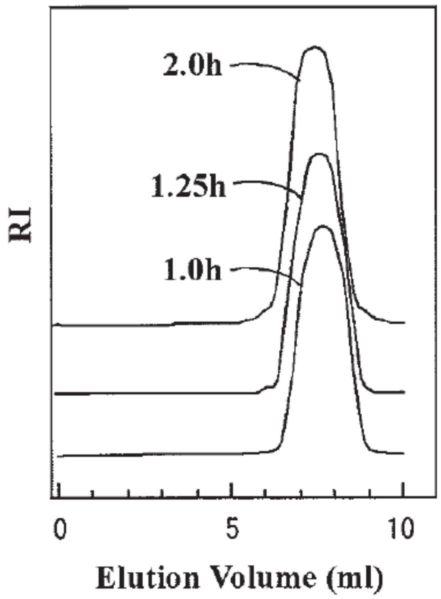


Table 1. Polymerization Conditions and Results for Photopolymerizations of MA[a]

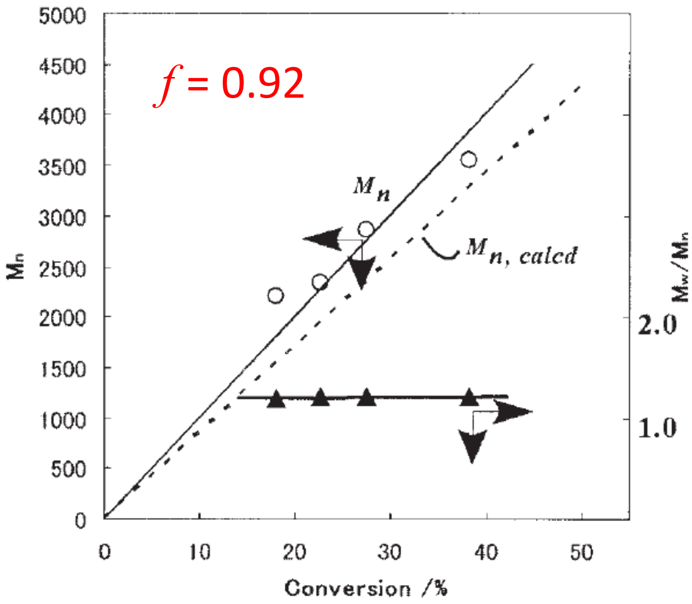
Expt No.	Irradiation Time (h)	Conversion[b] (%)	M_n[c]	M_w/M_n[d]
1	0.75	17.7	2250	1.20
2	1.0	22.6	2350	1.21
3	1.25	27.4	2850	1.21
4	2.0	38.1	3550	1.21

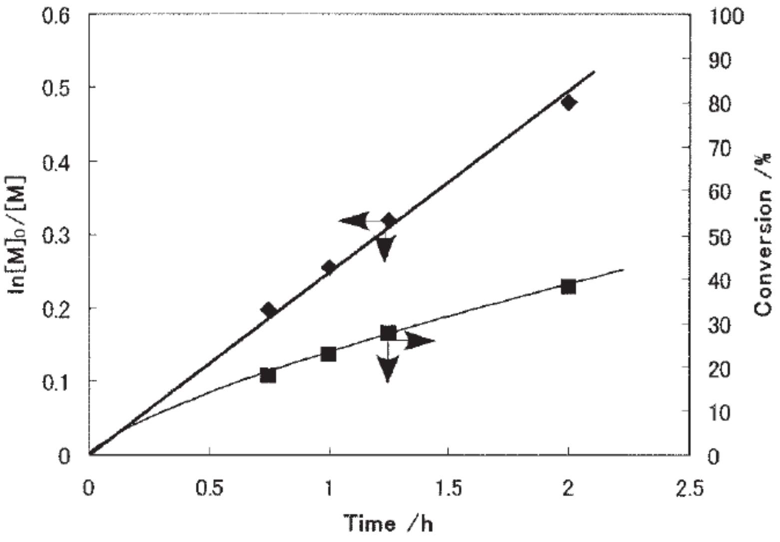
[a] Polymerized in methanol (30 vol % MA solution) initiated by CDPA as iniferter ($[MA]_0/[CDPA]_0 = 100$) under UV irradiation at 30 °C.

[b] Determined by gravimetric measurements.

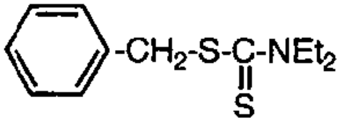
[c] Determined by intrinsic viscosity in methanol at 26 °C.

[d] Determined by GPC in methanol as eluent using calibration for PEO standard samples.

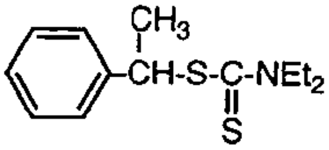

f = 0.92



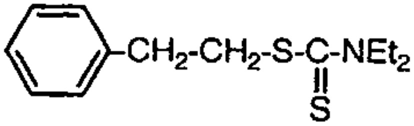
*Ishizu et al., J. Polym. Sci. Part A, 43, 230 (**2005**)*



BDC



StDC



PEDC

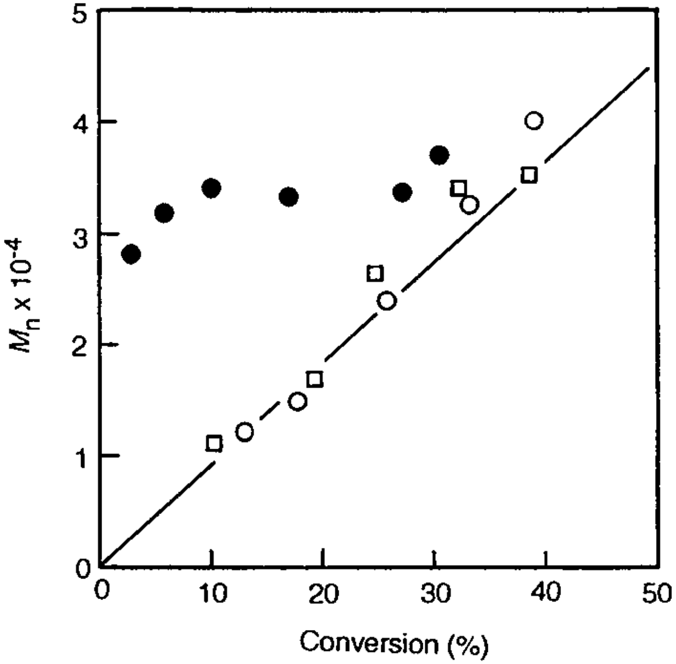


Figure 2. Conversion–M_n relationships of the polymer obtained from polymerization of St with (○) BDC, (□) StDC, and (●) PEDC. Polymerization conditions are identical to those in Figure 1. The line indicates calculated one from $M_n = 104.2 \times [\mathrm{St}]/[\mathrm{RDC}] \times \text{conversion}\ (\%)/100$.

*Doi et al., J. Polym. Sci. Part A, 32, 2241 (**1994**)*

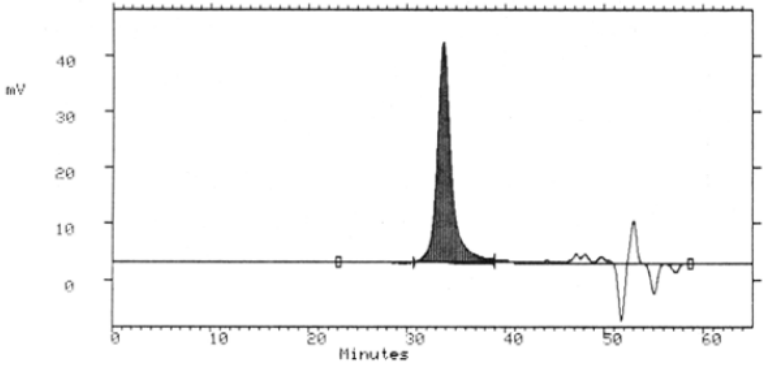
Nitroxide Mediated Polymerization

Narrow Molecular Weight Resins by a Free-Radical Polymerization Process

Michael K. Georges,* Richard P. N. Veregin, Peter M. Kazmaier, and Gordon K. Hamer

Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario, Canada L5K 2L1

Received January 11, 1993



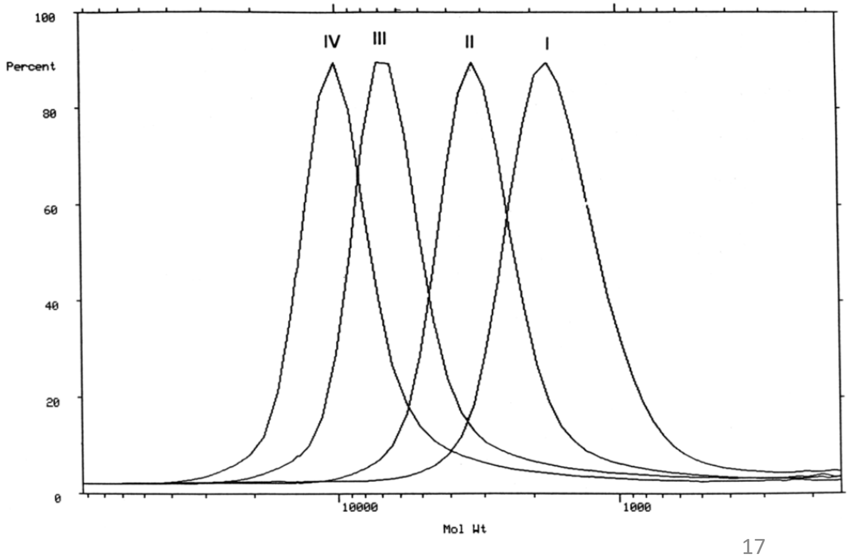
```
Number Average          7873          Weight Average          9989
Peak Molecular Weight   10273         Dispersity              1.268785
Z avg / W avg           1.174933
```

Table I. Polymerization of Styrene (TEMPO/BPO = 1.2)

sample	convn (%)	rxn time (h)	M_n (10^{-3})	M_w (10^{-3})	PD
I	20	21	1.7	2.2	1.28
II	51	29	3.2	4.1	1.27
III	76	45	6.8	8.2	1.21
IV	90	69	7.8	10.0	1.27

Table II. Polymerization of Styrene as a Function of the TEMPO/BPO Ratio

sample	TEMPO/BPO	convn (%)	M_n (10^{-3})	M_w (10^{-3})	PD
I	0.5	86	45.6	71.7	1.57
II	1.5	74	33.1	41.1	1.24
III	3.0	71	18.2	21.7	1.19



Molecular Weight Control by a "Living" Free-Radical Polymerization Process

Craig J. Hawker

IBM Almaden Research Center, 650 Harry Road
San Jose, California 95120-6099

Received July 8, 1994

Table 1. Comparison of GPC Molecular Weights with Calculated Molecular Weights for Polystyrenes, **3**

M_n (exptl)	M_n (calcd)	PD[a]	M_n (exptl)	M_n (calcd)	PD[a]
3 450	3 330	1.15	54 500	59 500	1.29
4 900	5 200	1.14	82 000	90 500	1.36
13 000	13 500	1.10	110 000	123 000	1.41
25 500	28 000	1.20			

[a] Polydispersity.

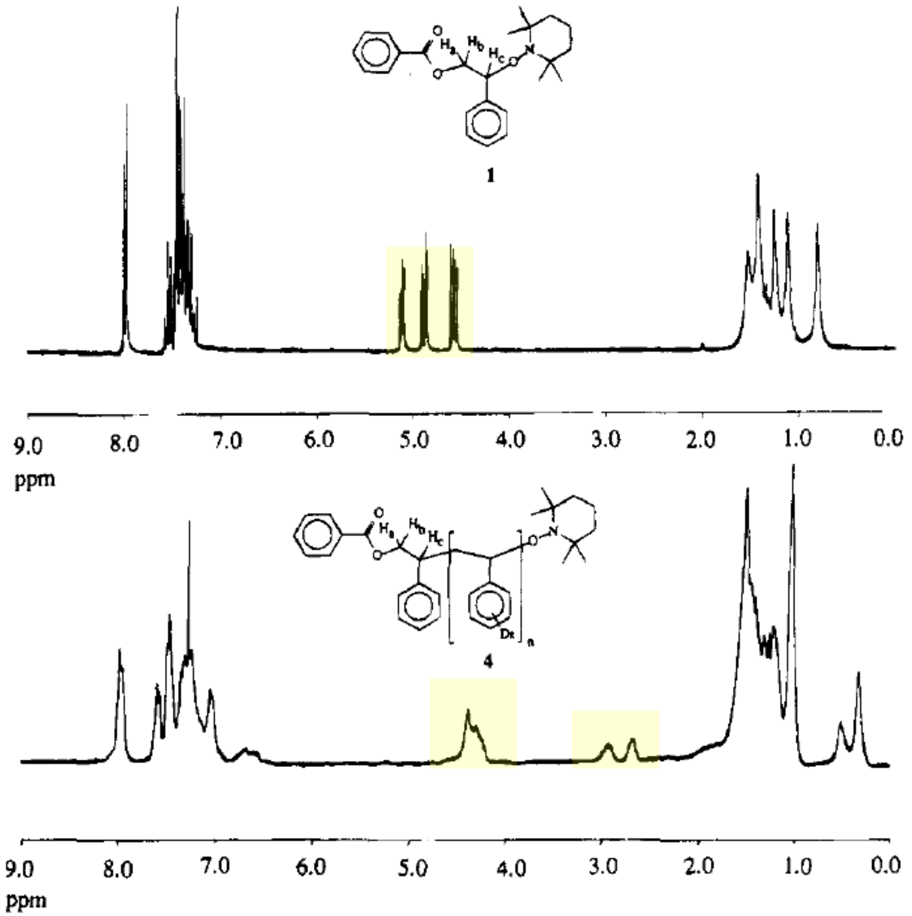
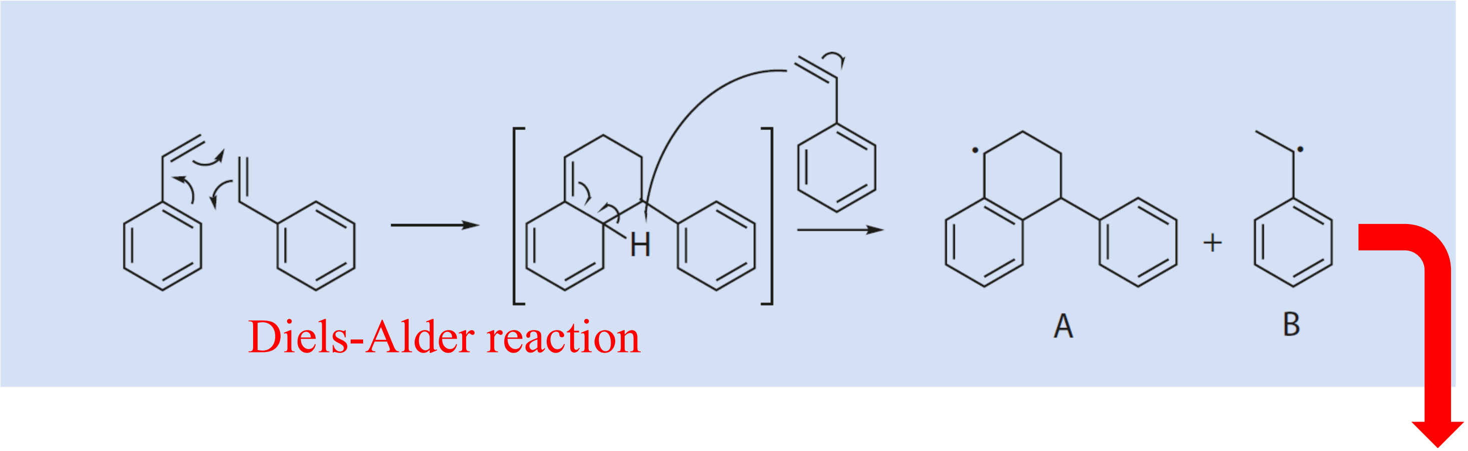


Figure 1. Comparison of the 300 MHz ^{1}H NMR spectra of modified initiator, **1**, and polymer obtained after reaction with styrene-d_8, **4**.

auto-polimerizzazione (anche chiamata thermal initiation) di St:



polimerizzazione

Only proven to occur with styrene.

- Mechanism involves preliminary dimer formation (via Diels-Alder reaction of two monomers), followed by hydrogen atom transfer to a third monomer.

Use of additives for NMP:

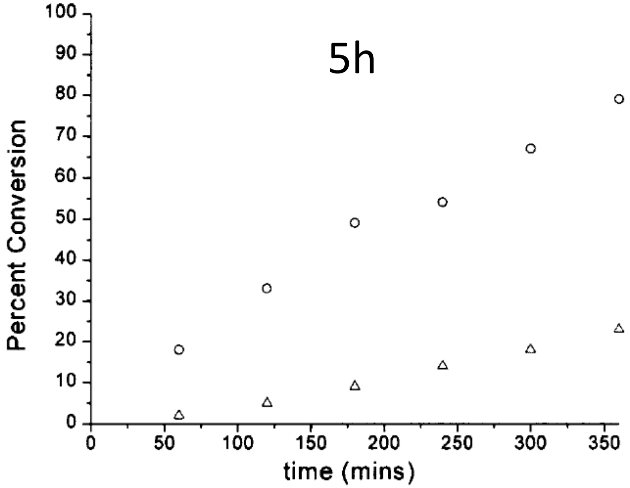


Figure 1. Percentage conversion as a function of time for the polymerization of styrene with **6** using (a) no additive (△) and (b) 10 weight percent of **7** (⊙).

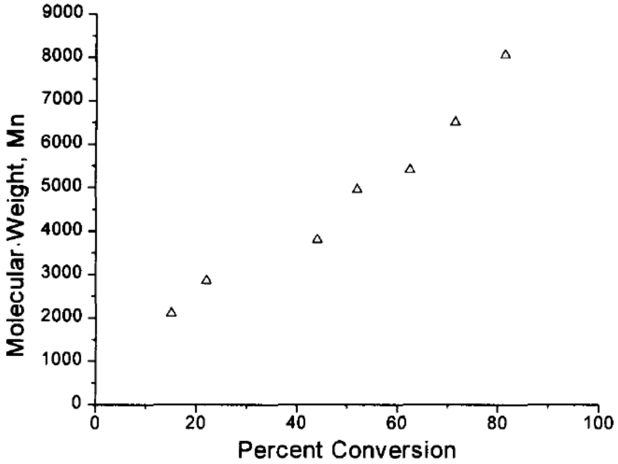
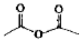
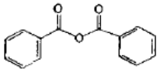
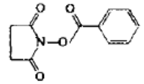
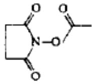
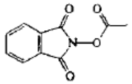
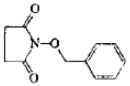
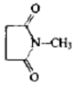
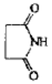
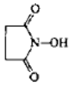
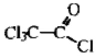
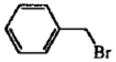


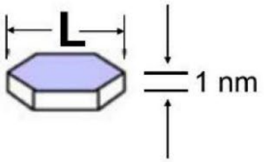
Figure 2. Evolution of molecular weight, M_n, with the percentage conversion for the polymerization of styrene at 123°C initiated by **6** using 10 wt% of **7** as an additive.

Table 1. Effect of additive on nitroxide mediated 'living' free radical polymerization

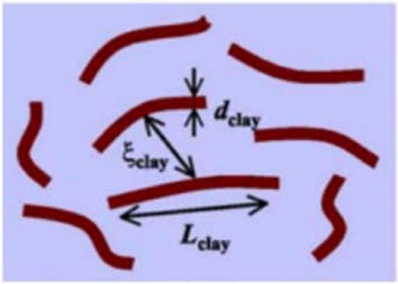
No.	Additive	Effect
16		+
17		+
7		+
8		+
9		+
10		-
13		-
14		-
15		-
18	 $Cl_3C-C(=O)Cl$	+
19		-
20	Me_2SO_4	+

Polymer NANOCOMPOSITES:

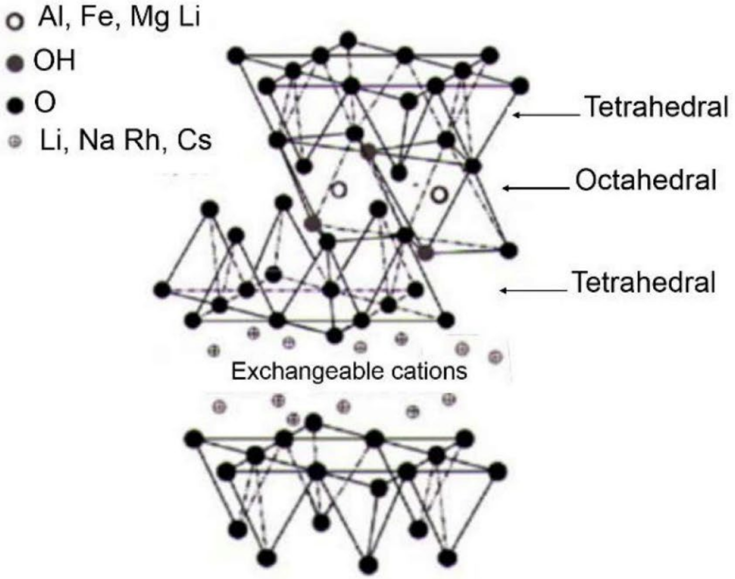
Diverse applications in automotive industry and aerospace materials.



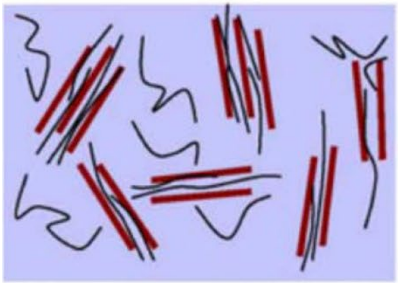
One Clay Platelet
L: 100 – 200 nm in case of MMT



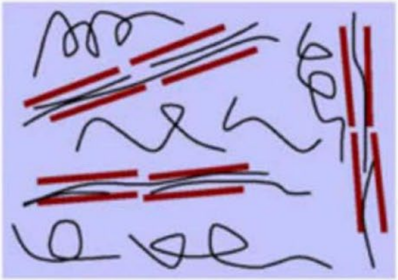
Form factors of dispersed clay



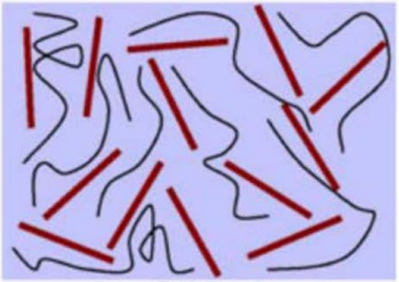
The structure of 2:1 layered silicates



Intercalated



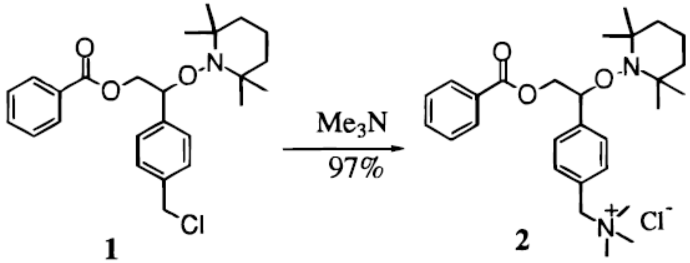
Intercalated-and-flocculated



Exfoliated

Direct Synthesis of Dispersed Nanocomposites by in Situ Living Free Radical Polymerization Using a Silicate-Anchored Initiator

Marc W. Weimer,[†] Hua Chen,[‡] Emmanuel P. Giannelis,[‡] and Dotsevi Y. Sogah*,[†]



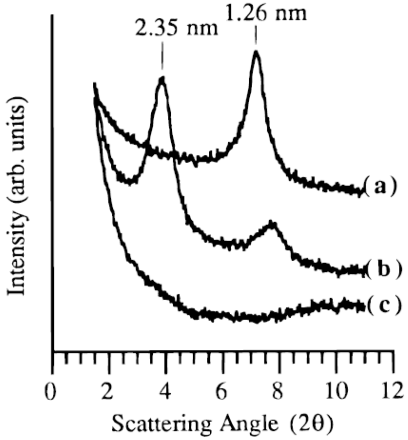


Figure 1. Plot of X-ray diffraction intensity (in arbitrary units) versus scattering angle (in degrees). (a) Original layered silicate. (b) Silicate-anchored initiator **3a**. (c) PS-silicate nanocomposite **4a**.

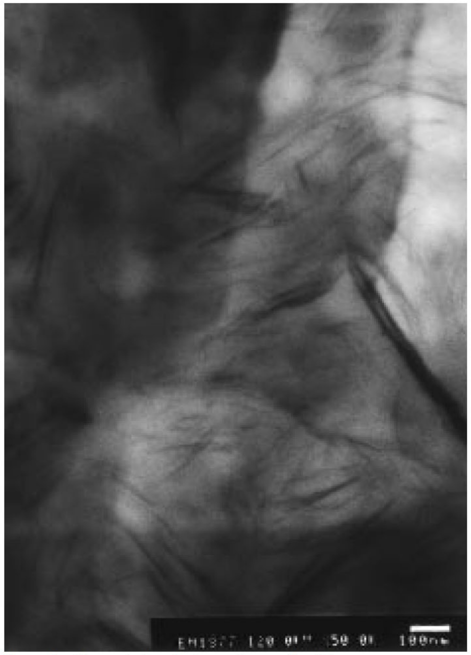
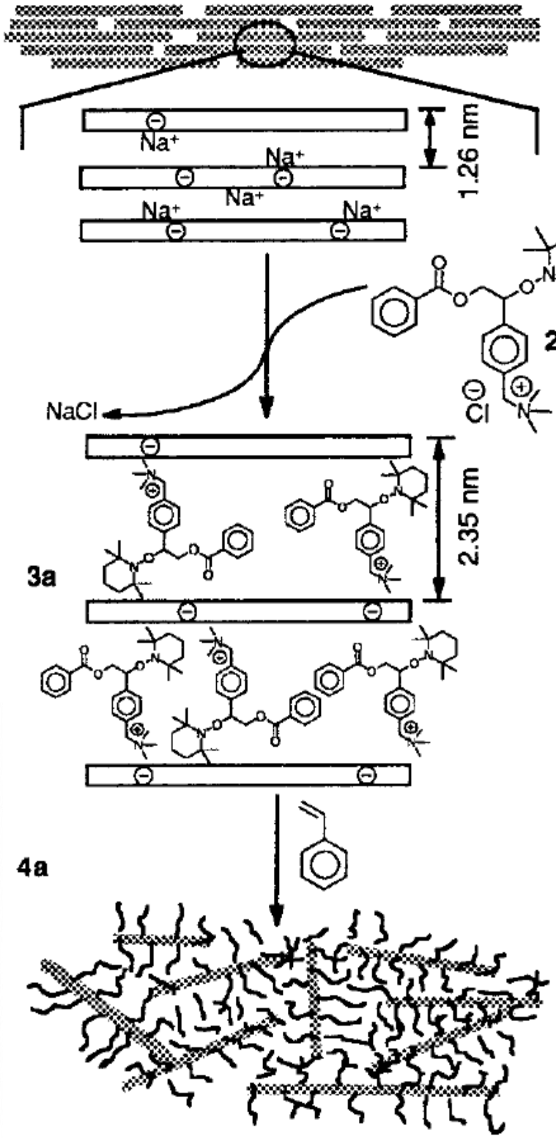


Figure 2. Transmission electron micrograph of **4a**.



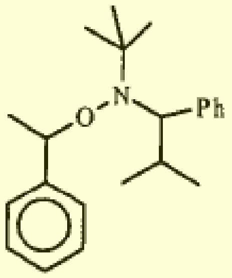
“Universal” Alkoxyamines

Development of a Universal Alkoxyamine for “Living” Free Radical Polymerizations

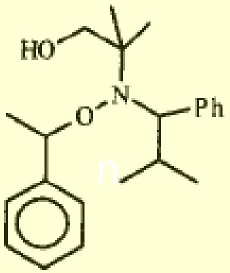
Didier Benoit,[†] Vladimir Chaplinski,[‡] Rebecca Braslau,*[,‡] and Craig J. Hawker*[,†]

Table 1. Molecular Weight, M_n, and Polydispersity of Product Obtained from the Bulk Polymerization of 200 Equiv of Styrene, or *n*-Butyl Acrylate, with Various Alkoxyamines, at 123 °C

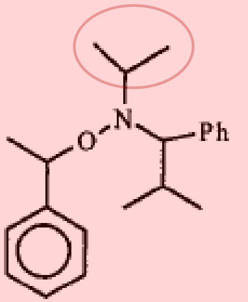
	polystyrene		poly(*n*-butyl acrylate)	
alkoxyamine	M_n	polydispersity	M_n	polydispersity
24	22 000	1.16	3 000	2.45
25	22 500	1.18	9 000	1.8
26	26 500	1.17	32 000	2.05
27	28 000	1.21	22 000	1.9
28	21 000	1.2	7 500	1.75
29	21 500	1.14	26 500	1.44
30a	33 000	1.71	41 500	2.52
30b	22 000	1.49	26 000	2.25
31	30 500	1.39	12 000	1.75
32	50 000	1.72	57 000	3.81
33	22 000	1.14	27 000	1.40
34	23 000	1.23	28 000	1.90
35	22 500	1.15	26 500	1.45
36	24 000	1.19	32 500	1.55
37	22 000	1.16	29 000	1.50
38	25 000	1.15	27 500	1.55
39	42 000	1.65	61 000	2.80
40	20 000	1.25	45 000	1.95
41	38 000	1.68	95 000	2.10
42	25 000	1.30	38 000	1.70



29



33



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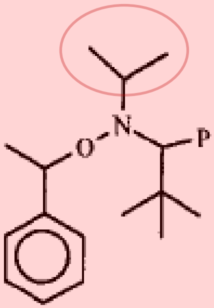
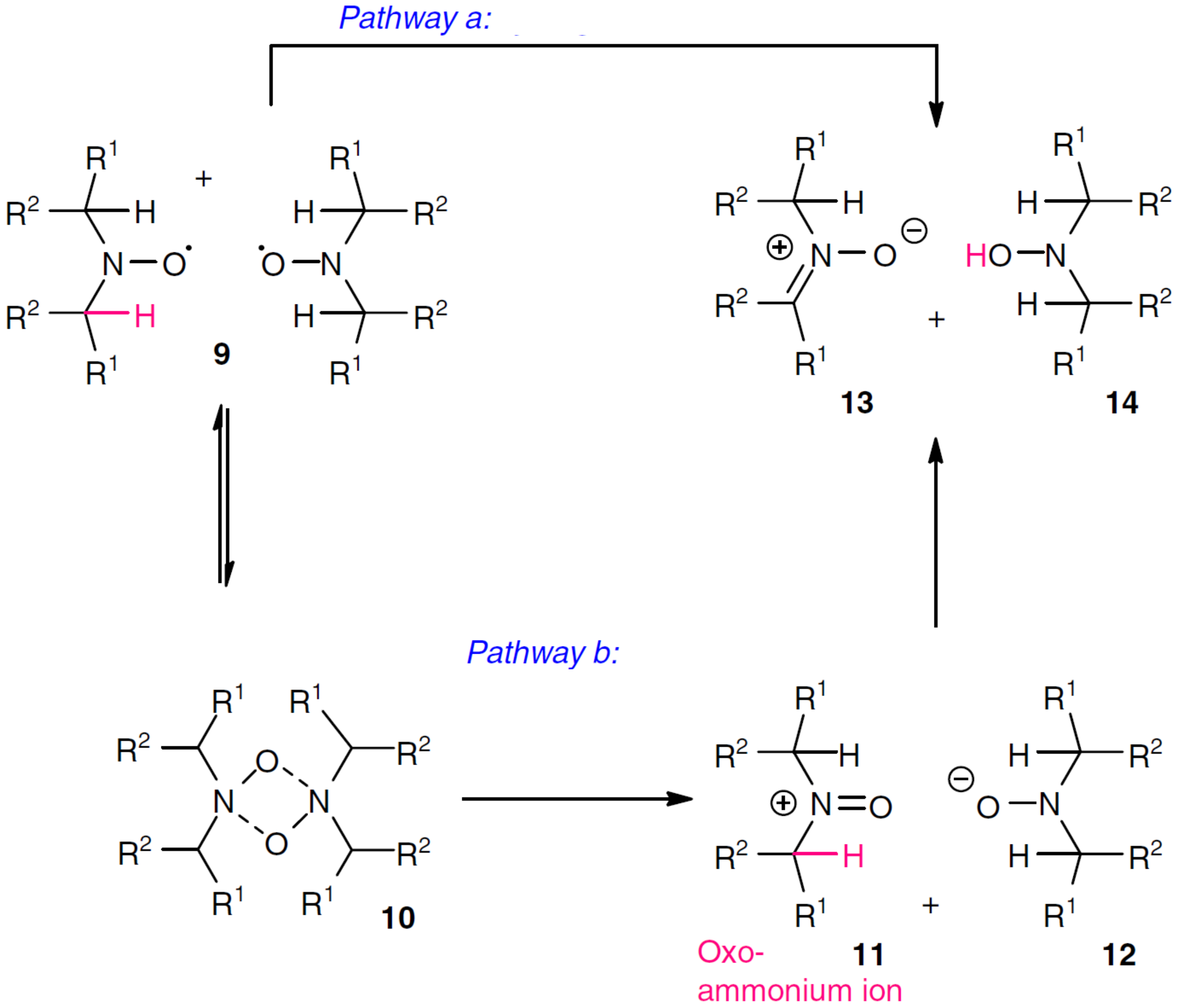
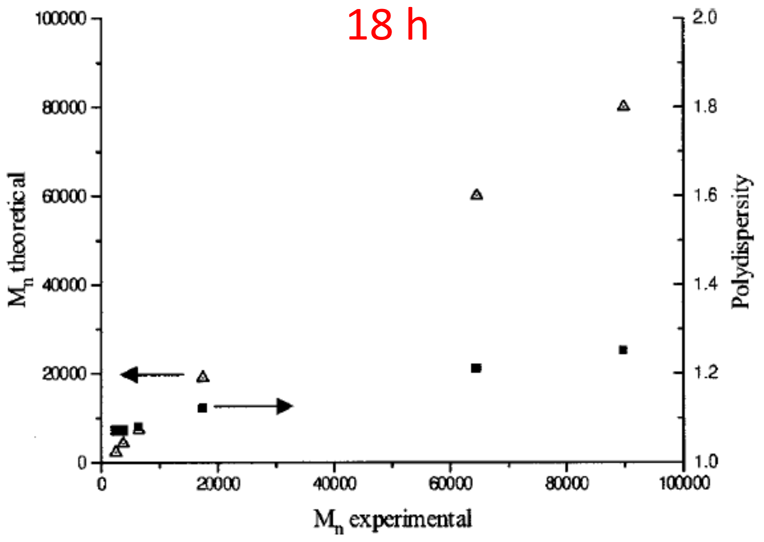


42


Pathway a:
9
13
14
10
Pathway b:
11
12
Oxo-
ammonium ion

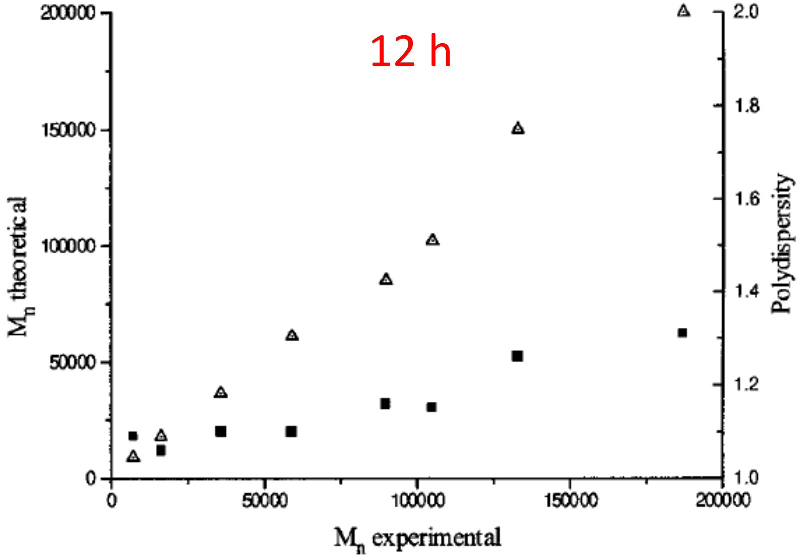
NMP of Styrene (bulk, 123°C)

without degassing and no purification of St



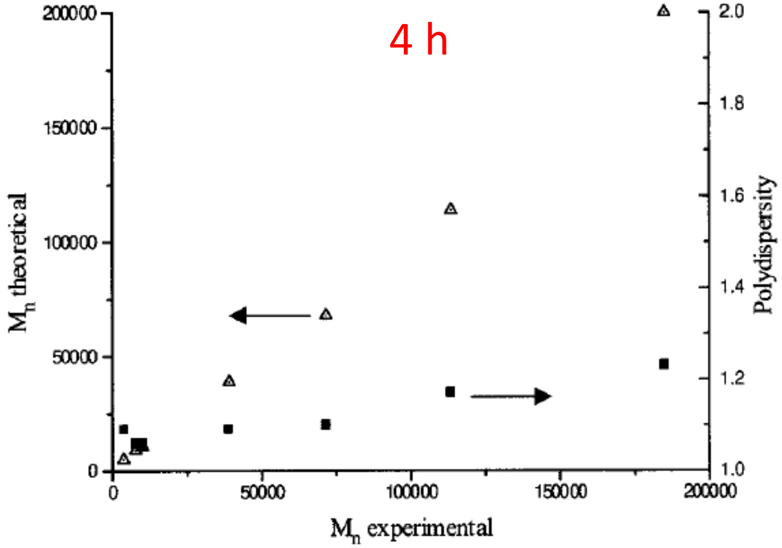
18 h

In the presence of 2 eq. of acetic anhydride



12 h

degassing and purifying St by distillation



4 h

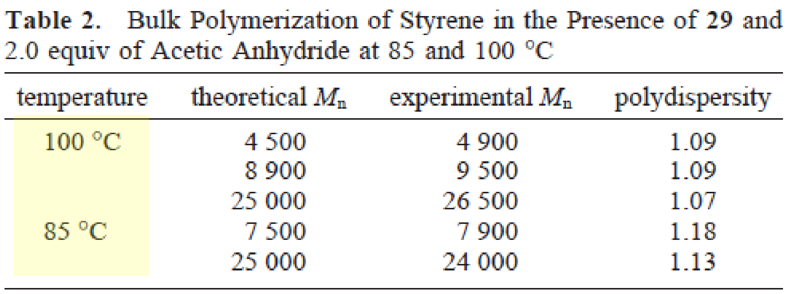


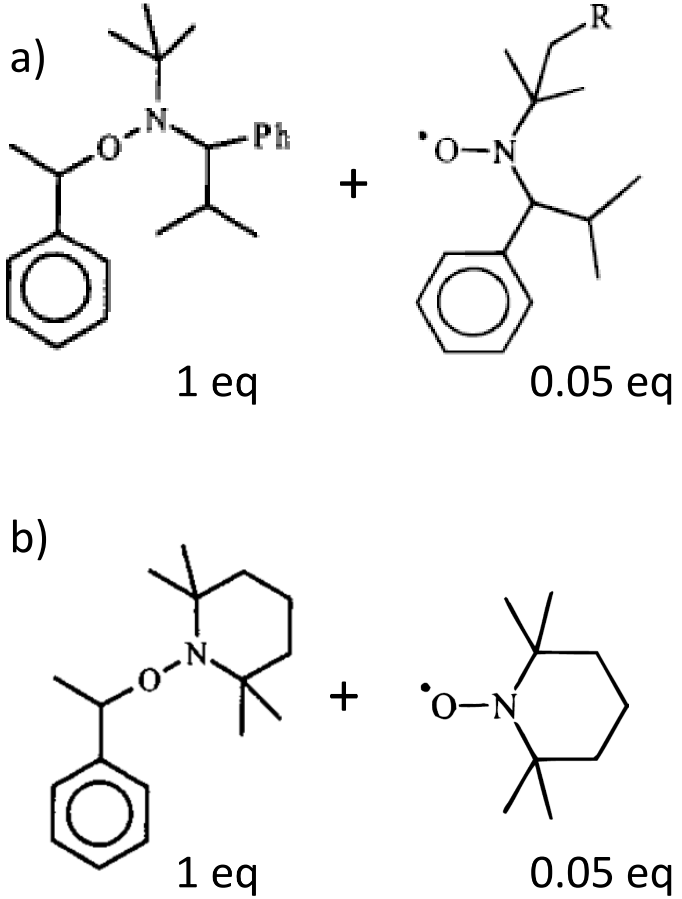
Table 2. Bulk Polymerization of Styrene in the Presence of 29 and 2.0 equiv of Acetic Anhydride at 85 and 100 °C

temperature	theoretical M_n	experimental M_n	polydispersity
100 °C	4 500	4 900	1.09
	8 900	9 500	1.09
	25 000	26 500	1.07
85 °C	7 500	7 900	1.18
	25 000	24 000	1.13

NMP of butyl acrylate (120°C)

Typical k_p for acrylates at 120°C: 11000 L mol^{-1} s^{-1} (k_p styrene: 1800 L mol^{-1} s^{-1})

*Polymerization is too fast (less controlled **PDI 1.5-2.2**) we need to slow it down:*



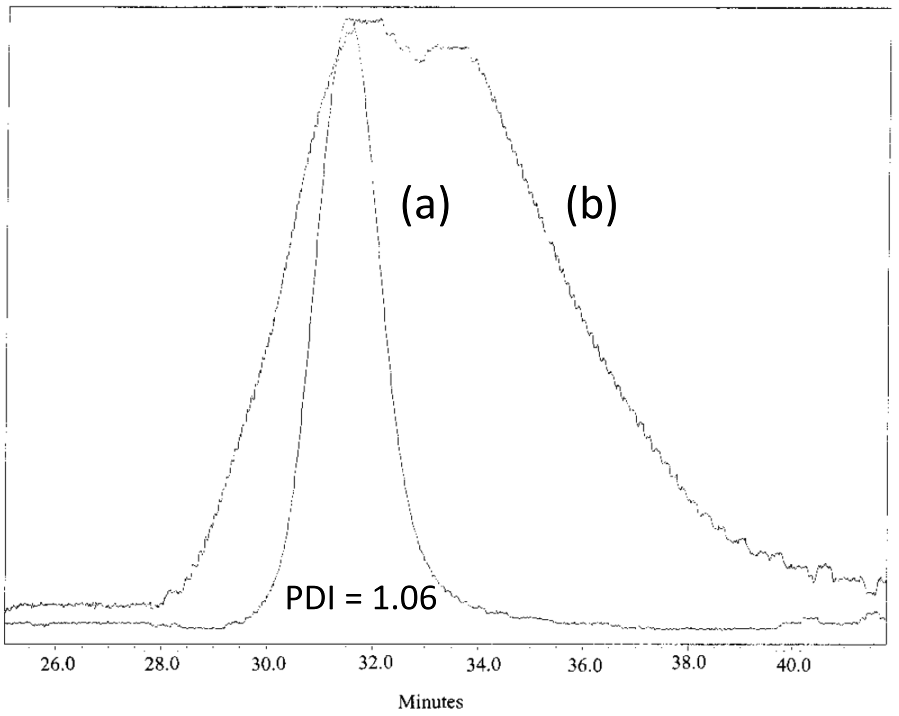
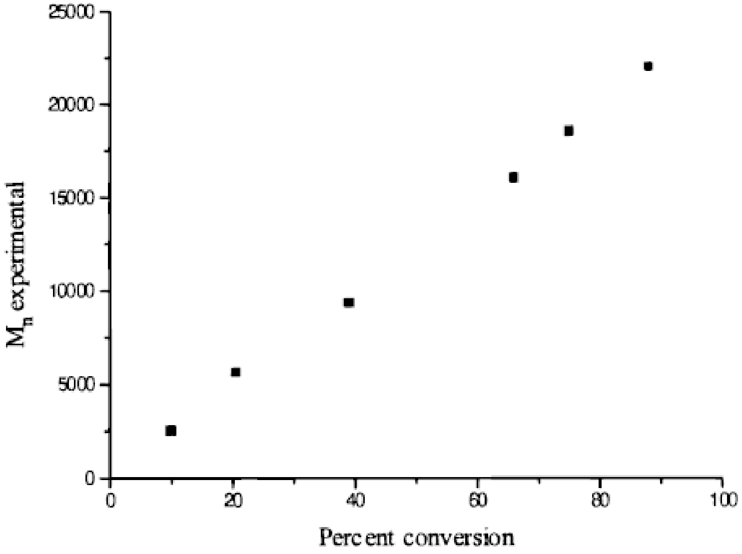
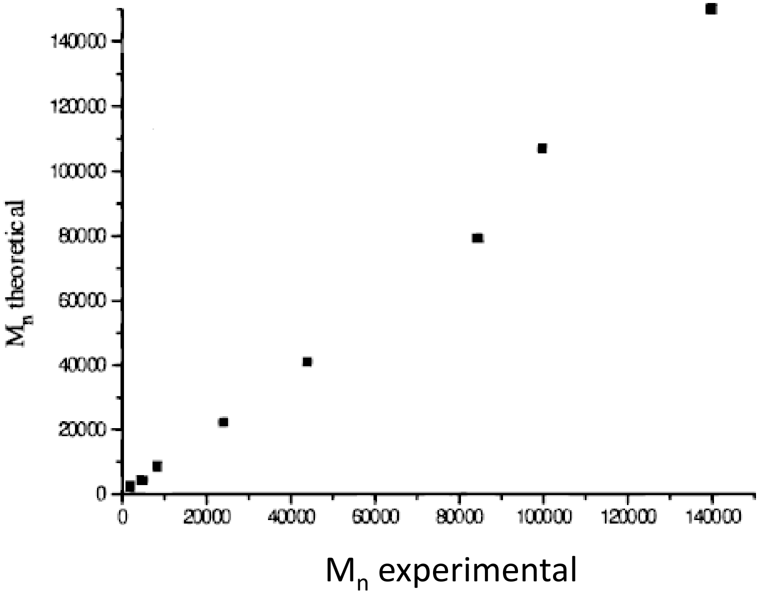


Figure 6. Comparison of GPC traces for poly(*n*-butyl acrylate) prepared by the polymerization of *n*-butyl acrylate (200 equiv) at 123 °C in the presence of (a) 1.0 equiv of **29** and 0.05 equiv of **1** and (b) 1.0 equiv of **24** and 0.05 equiv of TEMPO.


25000
20000
15000
10000
5000
0
M_n experimental
0
20
40
60
80
100
Percent conversion


140000
120000
100000
80000
60000
40000
20000
0
M_n theoretical
0
20000
40000
60000
80000
100000
120000
140000
M_n experimental

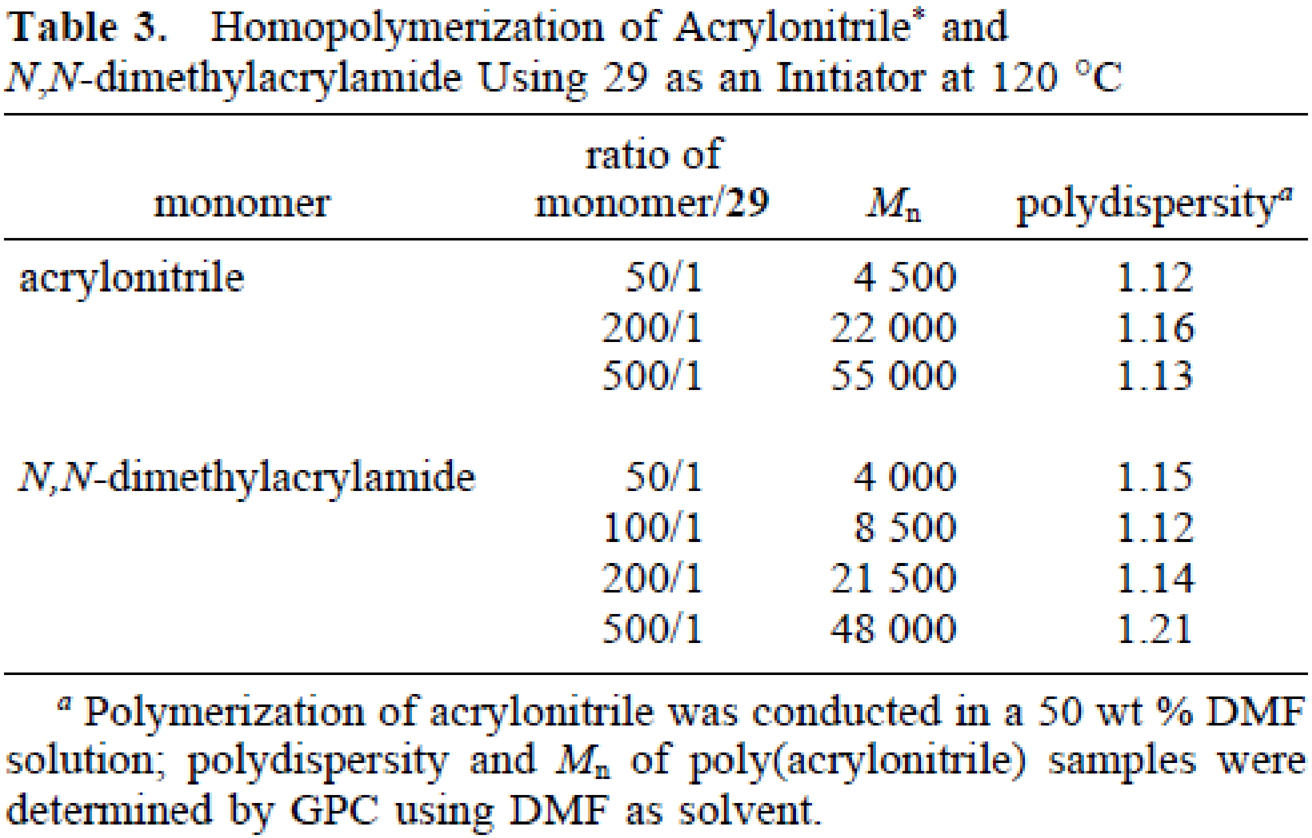
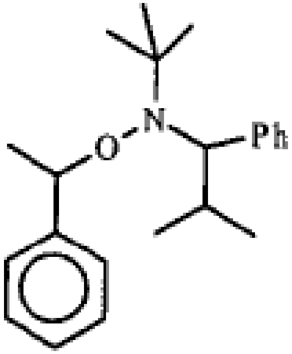


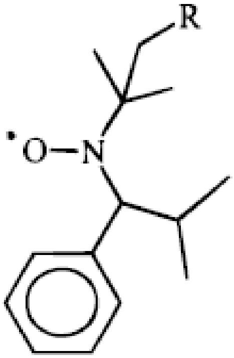
Table 3. Homopolymerization of Acrylonitrile* and *N,N*-dimethylacrylamide Using **29** as an Initiator at 120 °C

monomer	ratio of monomer/**29**	M_n	polydispersity[a]
acrylonitrile	50/1	4 500	1.12
	200/1	22 000	1.16
	500/1	55 000	1.13
N,N-dimethylacrylamide	50/1	4 000	1.15
	100/1	8 500	1.12
	200/1	21 500	1.14
	500/1	48 000	1.21

[a] Polymerization of acrylonitrile was conducted in a 50 wt % DMF solution; polydispersity and M_n of poly(acrylonitrile) samples were determined by GPC using DMF as solvent.

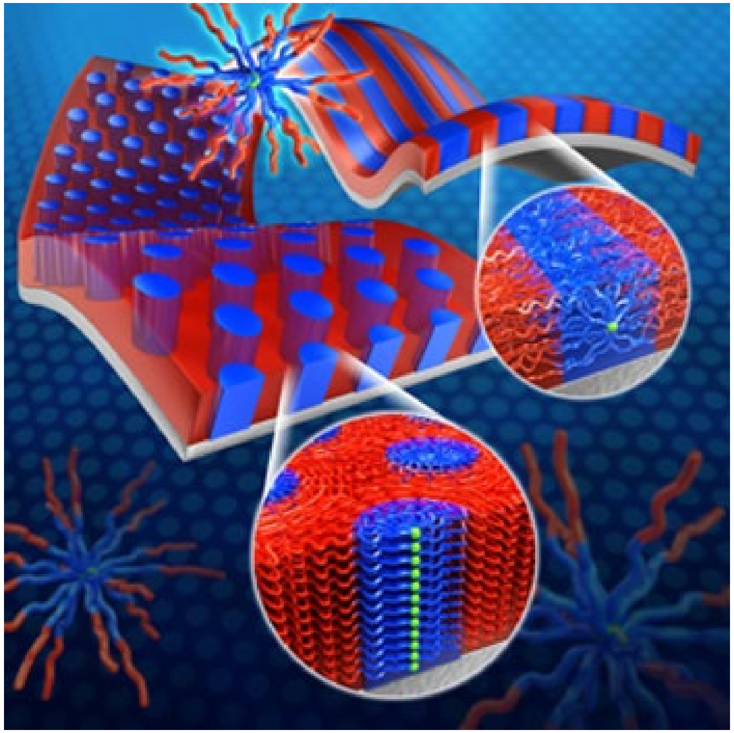


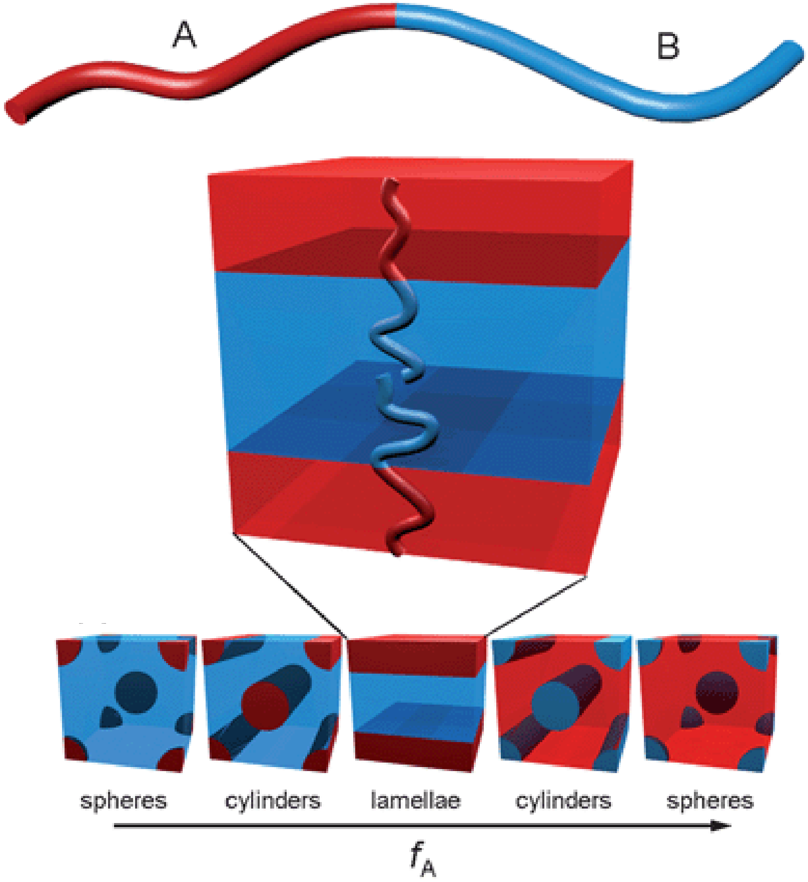
1 eq



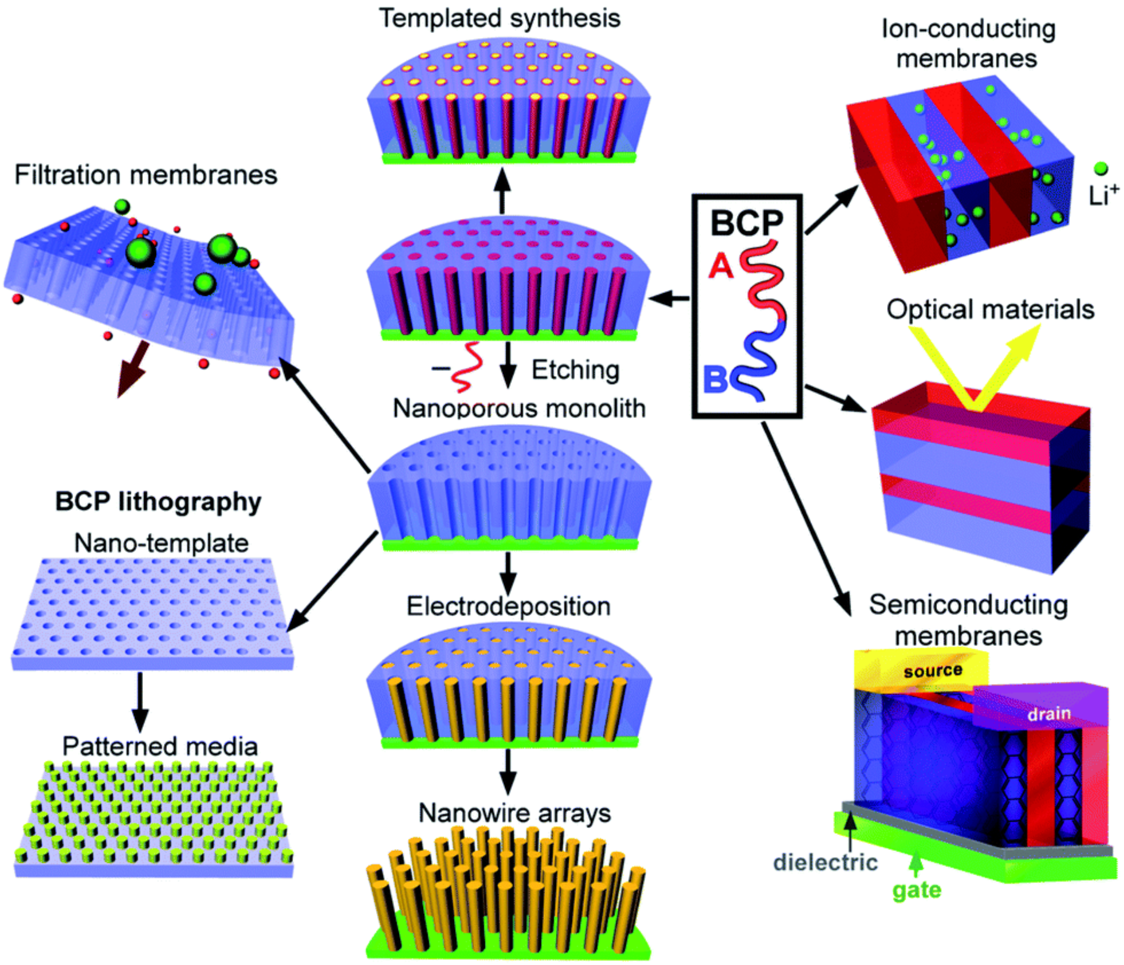
0.05 eq

Phase separation of well-defined block-copolymers

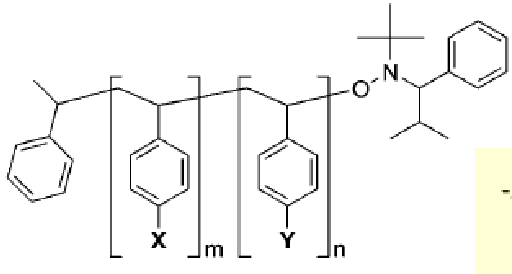




Block-copolymer lithographies:

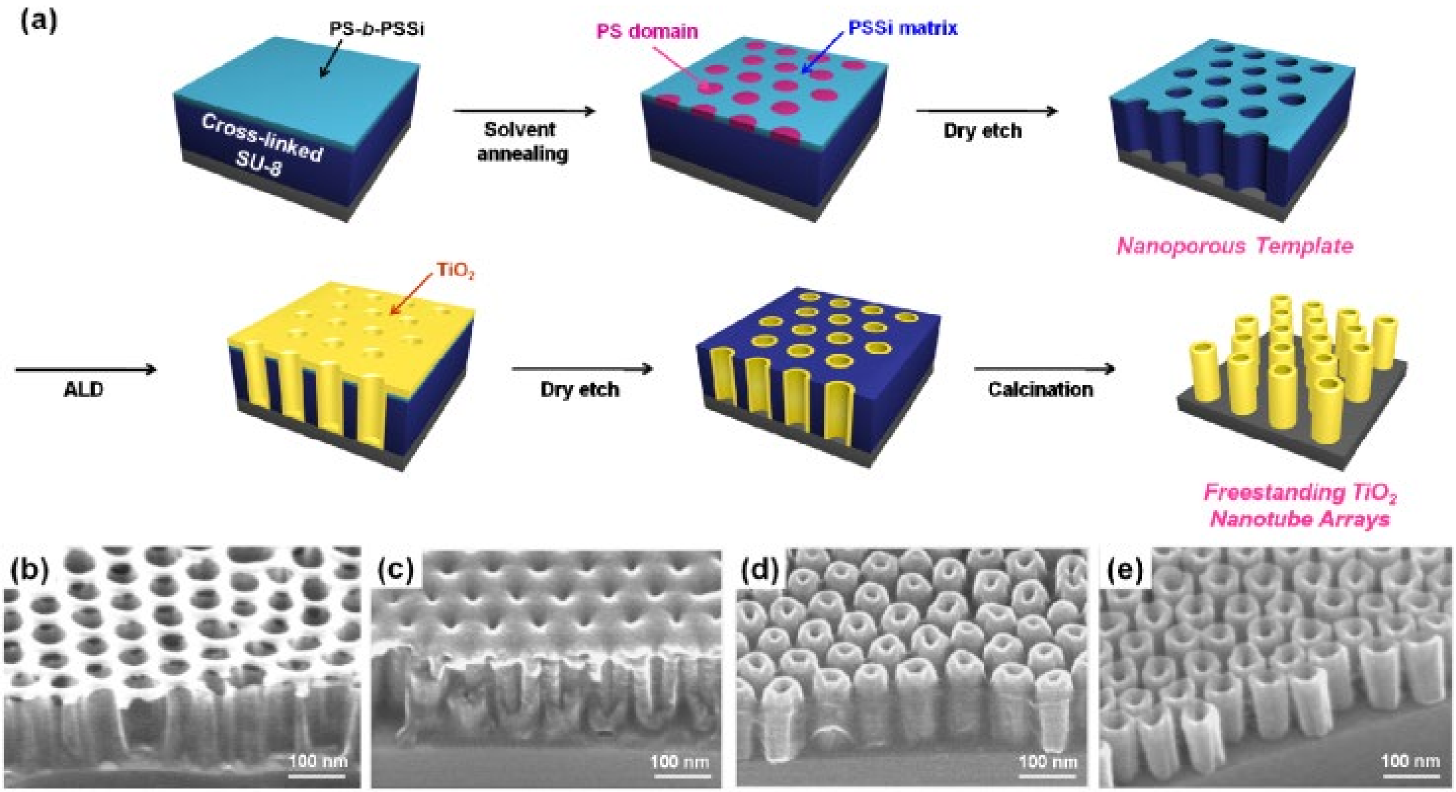


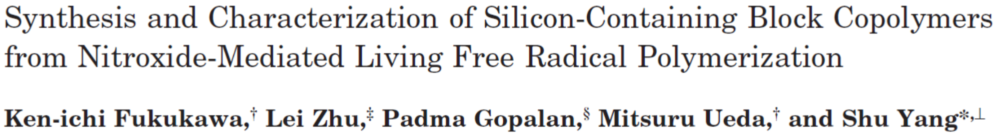
Block-copolymer lithography:



Block copolymer

-**X** or -**Y** = -H
$-Si(CH_3)_2Si(CH_3)_3$
$-CH\{Si(CH_3)_3\}_2$
$-CH_2Si(CH_3)_2OSi(CH_3)_3$
$-OC{=}OCH_3$





Synthesis and Characterization of Silicon-Containing Block Copolymers from Nitroxide-Mediated Living Free Radical Polymerization

Ken-ichi Fukukawa,[†] Lei Zhu,[‡] Padma Gopalan,[§] Mitsuru Ueda,[†] and Shu Yang*,[⊥]

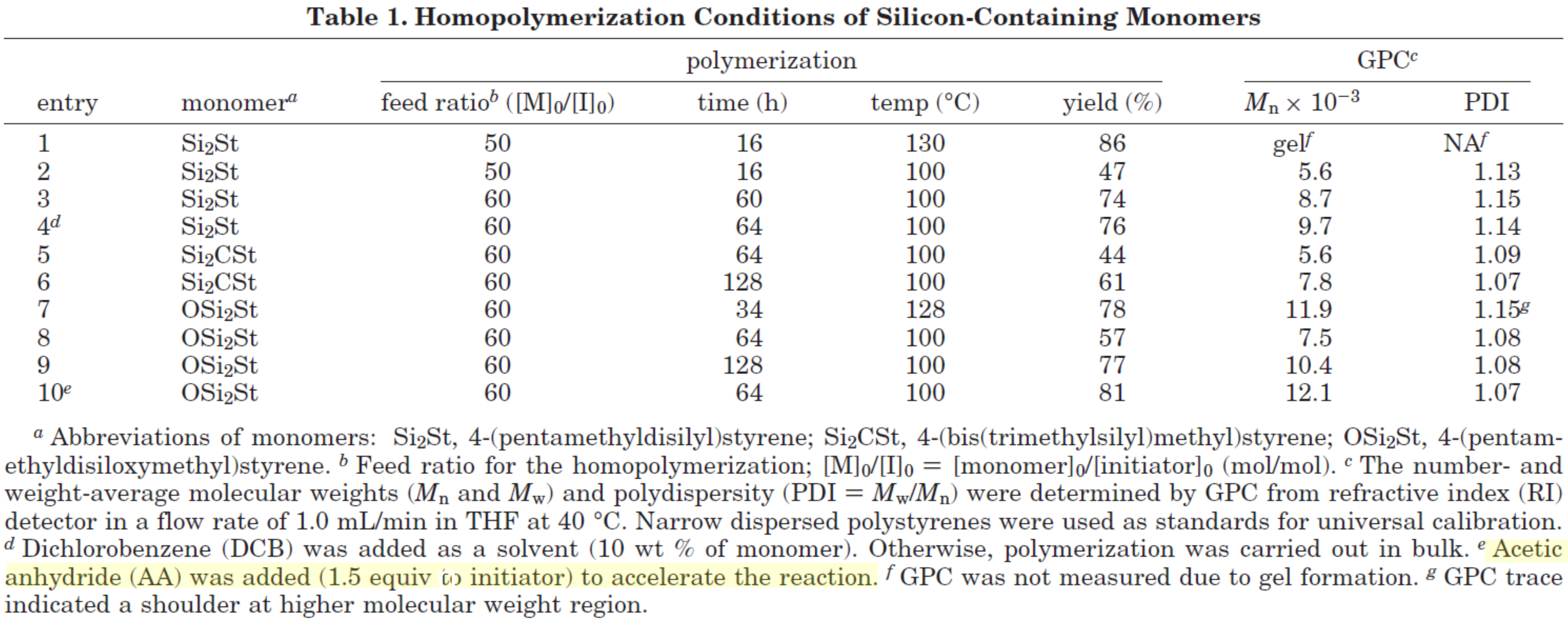
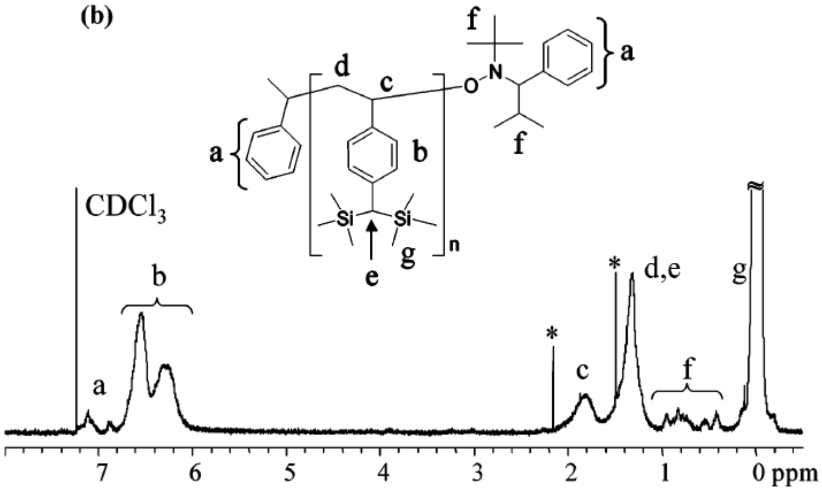


Table 1. Homopolymerization Conditions of Silicon-Containing Monomers

		polymerization				GPC[c]	
entry	monomer[a]	feed ratio[b] ($[M]_0/[I]_0$)	time (h)	temp (°C)	yield (%)	$M_n \times 10^{-3}$	PDI
1	Si_2St	50	16	130	86	gel[f]	NA[f]
2	Si_2St	50	16	100	47	5.6	1.13
3	Si_2St	60	60	100	74	8.7	1.15
4[d]	Si_2St	60	64	100	76	9.7	1.14
5	Si_2CSt	60	64	100	44	5.6	1.09
6	Si_2CSt	60	128	100	61	7.8	1.07
7	OSi_2St	60	34	128	78	11.9	1.15[g]
8	OSi_2St	60	64	100	57	7.5	1.08
9	OSi_2St	60	128	100	77	10.4	1.08
10[e]	OSi_2St	60	64	100	81	12.1	1.07

[a] Abbreviations of monomers: Si_2St, 4-(pentamethyldisilyl)styrene; Si_2CSt, 4-(bis(trimethylsilyl)methyl)styrene; OSi_2St, 4-(pentamethyldisiloxymethyl)styrene. [b] Feed ratio for the homopolymerization; $[M]_0/[I]_0$ = $[\text{monomer}]_0/[\text{initiator}]_0$ (mol/mol). [c] The number- and weight-average molecular weights (M_n and M_w) and polydispersity (PDI = M_w/M_n) were determined by GPC from refractive index (RI) detector in a flow rate of 1.0 mL/min in THF at 40 °C. Narrow dispersed polystyrenes were used as standards for universal calibration. [d] Dichlorobenzene (DCB) was added as a solvent (10 wt % of monomer). Otherwise, polymerization was carried out in bulk. [e] Acetic anhydride (AA) was added (1.5 equiv to initiator) to accelerate the reaction. [f] GPC was not measured due to gel formation. [g] GPC trace indicated a shoulder at higher molecular weight region.



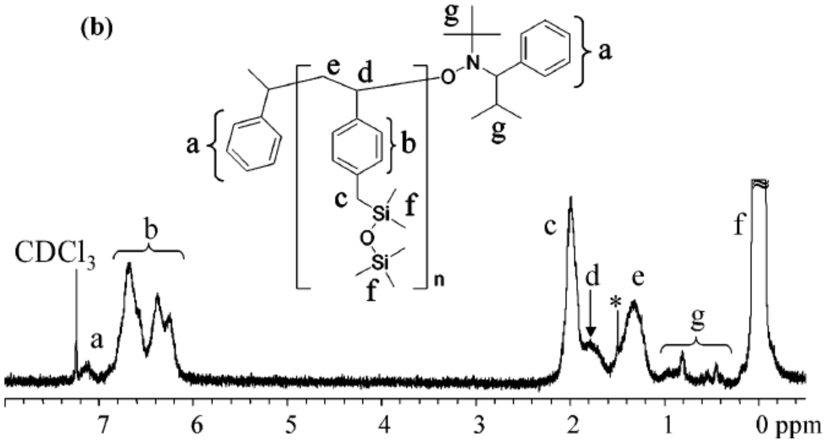
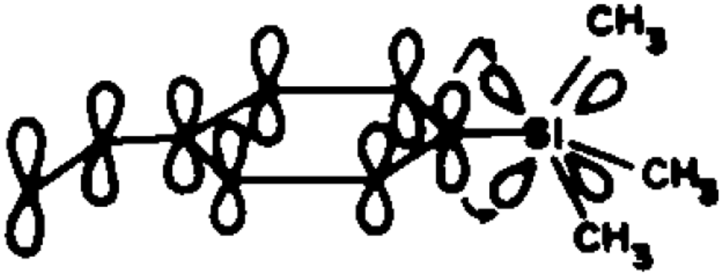
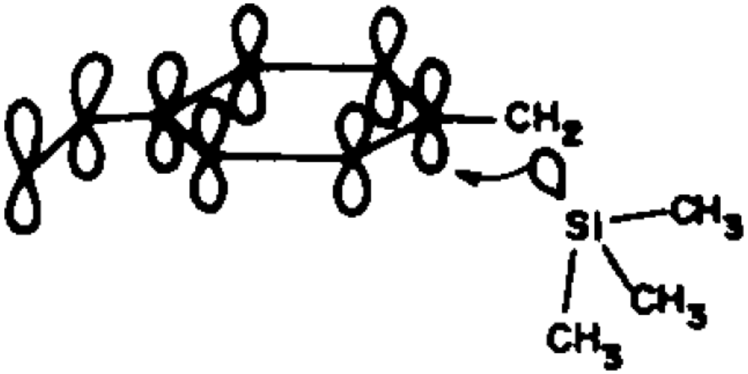


Table 2. Degree of Polymerization (DP_n) Calculated from ^1H NMR Data[a]

monomer[b]	M_n[c] × 10^{-3}	DP_n[d]	T_g[e] (°C)
St	3.5	32	99
AcOSt	5.0	36	122
Si_2St[f]	9.7	37	100
OSi_2St	7.5	23	0.5
Si_2CSt	5.6	21	122

AcOSt ≥ Si_2St > St > OSi_2St, Si_2CSt





The nature of the interaction of $\mathrm{C}-\mathrm{M}$ bonds ($\mathrm{M}=\mathrm{Si}$, Ge, Sn, or Pb) with aromatic Π-electron system is of great interest.[16-18] In compounds of the type $\mathrm{ArM(CH_3)_3}$ which has metal at α-position, there is net electron withdrawal from the aromatic Π-electron system.[19,20] While, in compounds of the type $\mathrm{ArCH_2M(CH_3)_3}$ which has metal at β-position, there is electron donation to the Π-electron system.[16,17,21] The former effect is most commonly attributed to $d_\Pi - p_\Pi$ interaction with the d-orbitals on M acting as Π-acceptors,[20,22,23] and the latter has been attributed to σ–Π hyperconjugation in which the polar $\mathrm{CH}_2^{\delta-}-\mathrm{M}^{\delta+}$ σ bond acts as a Π-electron source.[16,17]

Block-copolymerization:

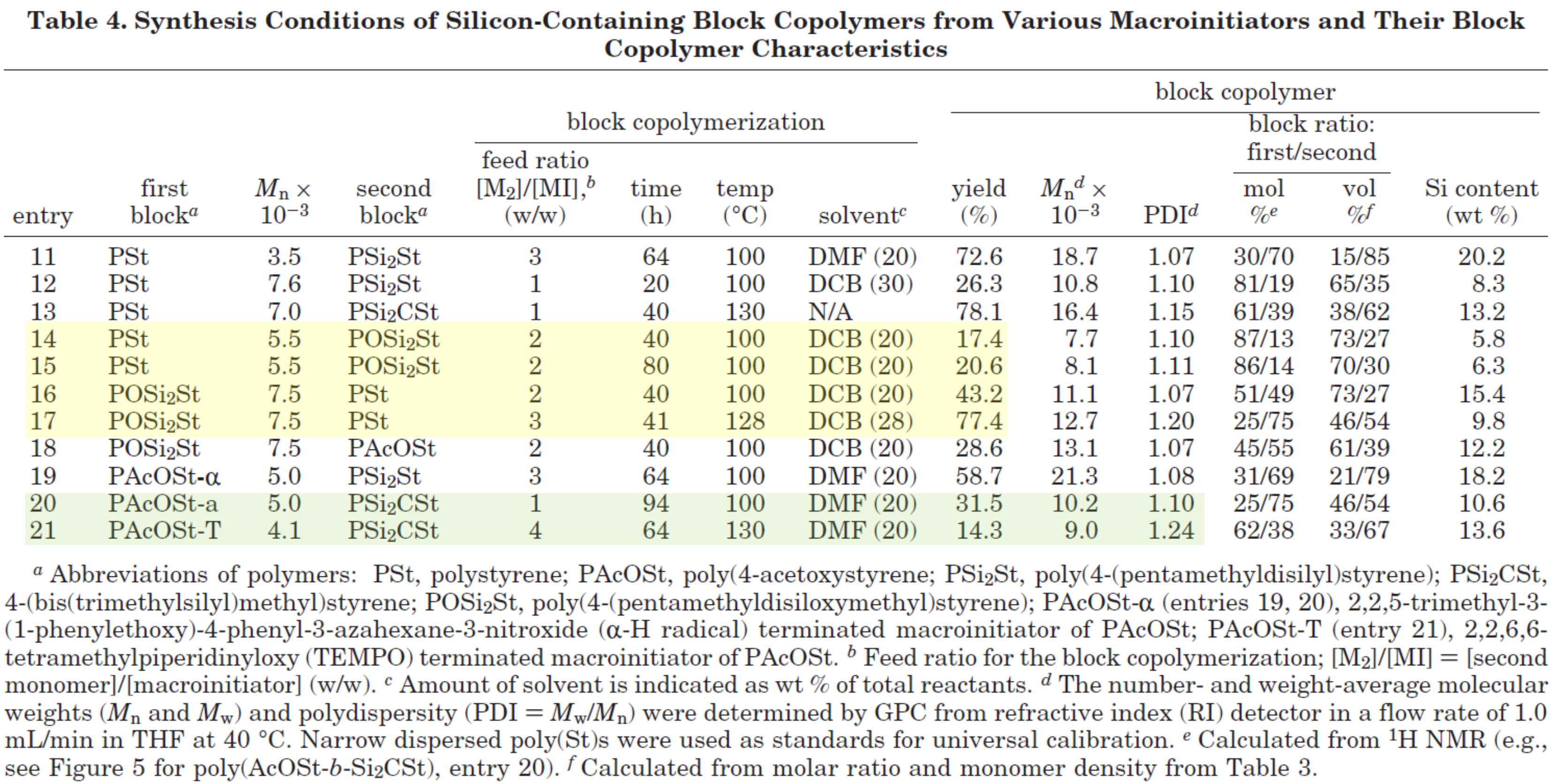
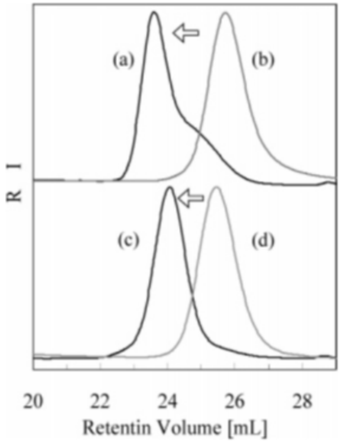


Table 4. Synthesis Conditions of Silicon-Containing Block Copolymers from Various Macroinitiators and Their Block Copolymer Characteristics

				block copolymerization				block copolymer					
											block ratio: first/second		
entry	first block[a]	$M_n \times 10^{-3}$	second block[a]	feed ratio $[M_2]/[MI]$,[b] (w/w)	time (h)	temp (°C)	solvent[c]	yield (%)	$M_n{}^d \times 10^{-3}$	PDI[d]	mol %[e]	vol %[f]	Si content (wt %)
11	PSt	3.5	PSi$_2$St	3	64	100	DMF (20)	72.6	18.7	1.07	30/70	15/85	20.2
12	PSt	7.6	PSi$_2$St	1	20	100	DCB (30)	26.3	10.8	1.10	81/19	65/35	8.3
13	PSt	7.0	PSi$_2$CSt	1	40	130	N/A	78.1	16.4	1.15	61/39	38/62	13.2
14	PSt	5.5	POSi$_2$St	2	40	100	DCB (20)	17.4	7.7	1.10	87/13	73/27	5.8
15	PSt	5.5	POSi$_2$St	2	80	100	DCB (20)	20.6	8.1	1.11	86/14	70/30	6.3
16	POSi$_2$St	7.5	PSt	2	40	100	DCB (20)	43.2	11.1	1.07	51/49	73/27	15.4
17	POSi$_2$St	7.5	PSt	3	41	128	DCB (28)	77.4	12.7	1.20	25/75	46/54	9.8
18	POSi$_2$St	7.5	PAcOSt	2	40	100	DCB (20)	28.6	13.1	1.07	45/55	61/39	12.2
19	PAcOSt-α	5.0	PSi$_2$St	3	64	100	DMF (20)	58.7	21.3	1.08	31/69	21/79	18.2
20	PAcOSt-a	5.0	PSi$_2$CSt	1	94	100	DMF (20)	31.5	10.2	1.10	25/75	46/54	10.6
21	PAcOSt-T	4.1	PSi$_2$CSt	4	64	130	DMF (20)	14.3	9.0	1.24	62/38	33/67	13.6

[a] Abbreviations of polymers: PSt, polystyrene; PAcOSt, poly(4-acetoxystyrene; PSi$_2$St, poly(4-(pentamethyldisilyl)styrene); PSi$_2$CSt, 4-(bis(trimethylsilyl)methyl)styrene; POSi$_2$St, poly(4-(pentamethyldisiloxymethyl)styrene); PAcOSt-α (entries 19, 20), 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane-3-nitroxide (α-H radical) terminated macroinitiator of PAcOSt; PAcOSt-T (entry 21), 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) terminated macroinitiator of PAcOSt. [b] Feed ratio for the block copolymerization; $[M_2]/[MI]$ = [second monomer]/[macroinitiator] (w/w). [c] Amount of solvent is indicated as wt % of total reactants. [d] The number- and weight-average molecular weights (M_n and M_w) and polydispersity (PDI = M_w/M_n) were determined by GPC from refractive index (RI) detector in a flow rate of 1.0 mL/min in THF at 40 °C. Narrow dispersed poly(St)s were used as standards for universal calibration. [e] Calculated from ^{1}H NMR (e.g., see Figure 5 for poly(AcOSt-*b*-Si$_2$CSt), entry 20). [f] Calculated from molar ratio and monomer density from Table 3.



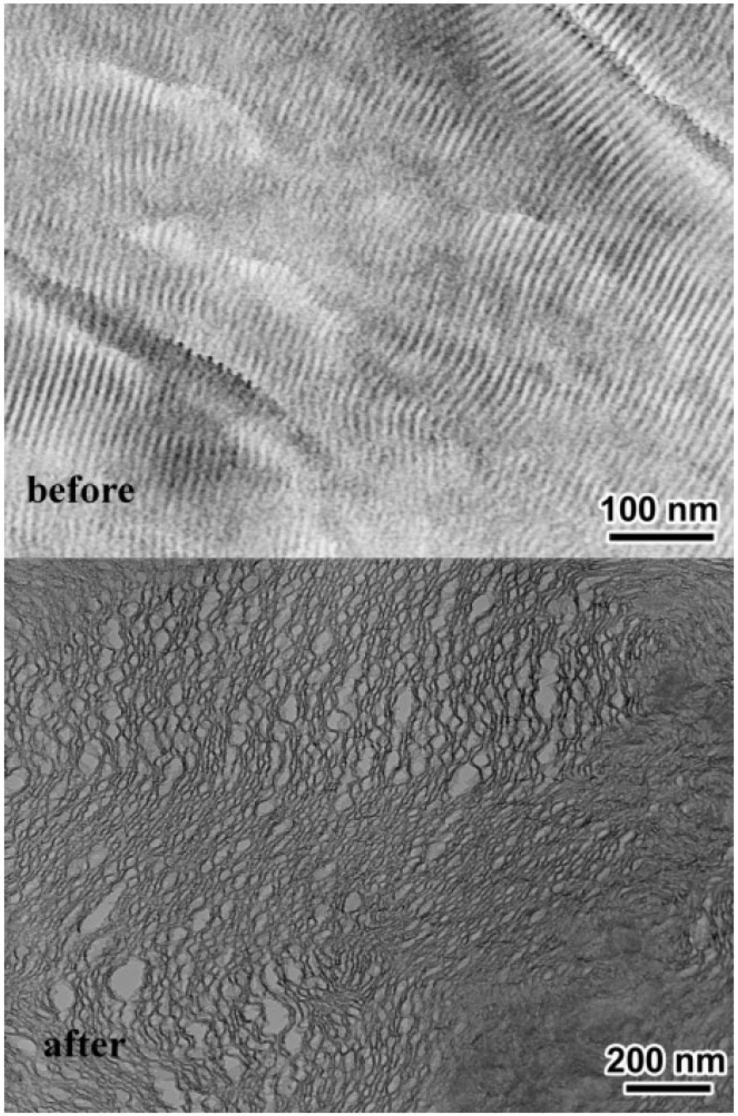


Figure 7. Transmission electron micrograph (TEM) images of PAcOSt−PSi$_2$CSt (46/54 v/v, entry 20 in Tables 4 and 5) before and after O$_2$ plasma for 5 min.

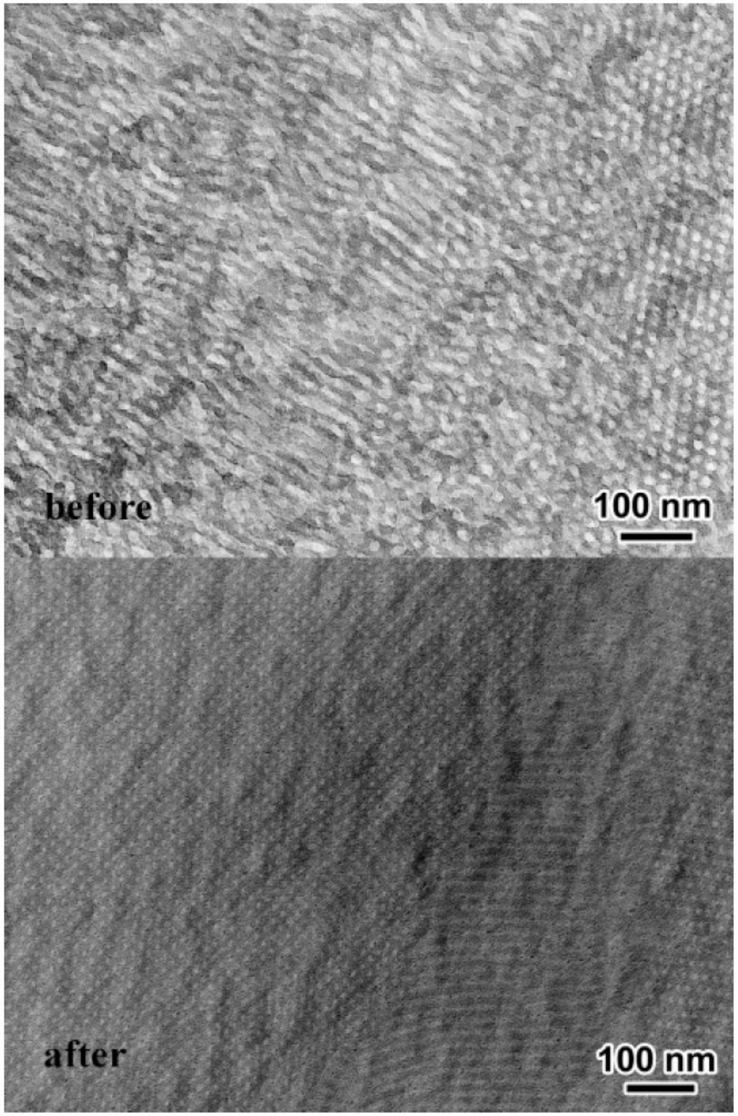


Figure 8. Transmission electron micrograph (TEM) images of PAcOSt−PSi$_2$St (21/79 v/v, entry 19 in Tables 4 and 5) before and after O$_2$ plasma for 10 min.