Probing the Side Chain Conformations of PyPEGMA Polymeric Brushes in Solution

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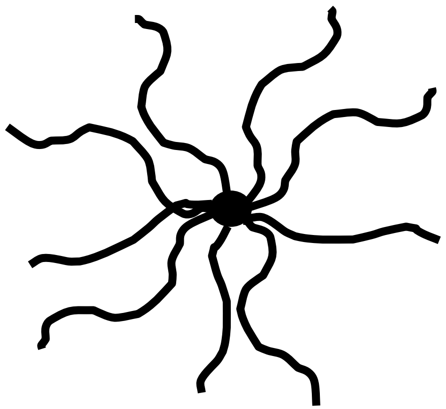
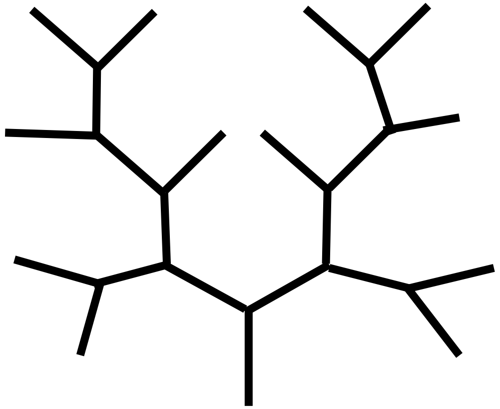
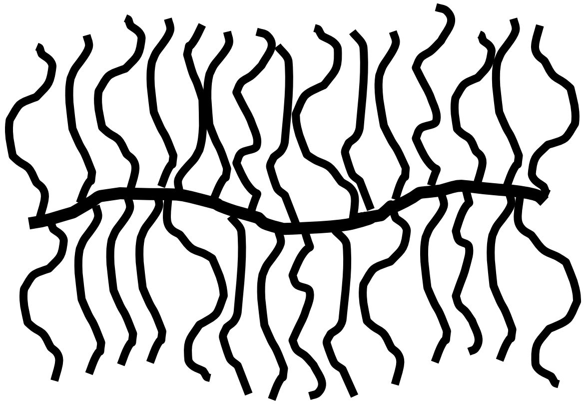
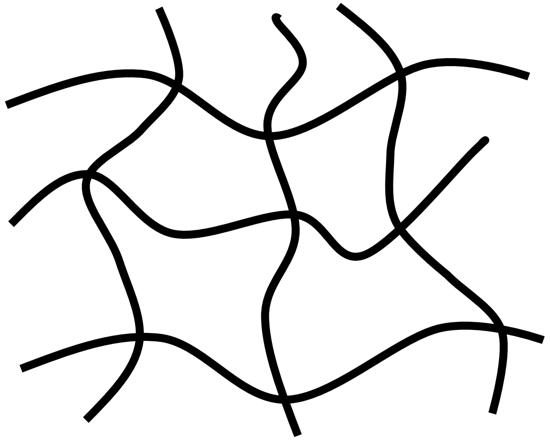
Outline

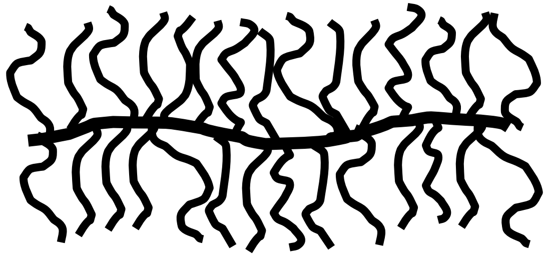
- Background
  - Polymers with Complex Architecture
  - Brush Polymers
- Fluorescence
  - Pyrene
  - Steady-State and Time Resolved Fluorescence
- Results
- Conclusions
- Future Work

Background

Polymers with complex architecture can be separated into 4 categories. These topologies include:

- Star
- Hyperbranched
- Brush
- Networks/ Gels



Brush Polymers

A polymeric bottle brush (PBB) is a highly branched macromolecule with a high degree of polymerization and high grafting density.

Currently PBBs are not synthesized commercially, however, there are a few promising applications.

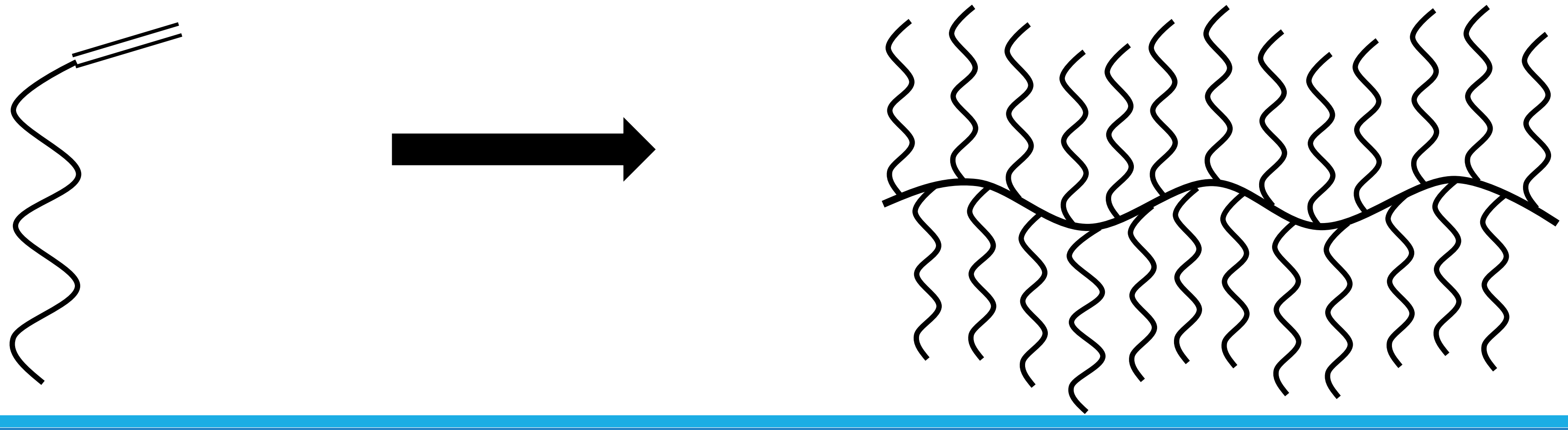
- Synthesis of super soft elastomers[1]
- Drug delivery systems[2]

1) Daniel, W. F. M.; Burdynska, J.; Vatankhah-Varnoosfaderani, M.; Matyjaszewski, K.; Paturej, J.; Rubinstein, M.; Dobrynin, A.V.; Sheiko, S. S. Solvent-Free, Supersoft and Superelastic Bottlebrush Melts and Networks. *Nat. Mater.* **2015**, *15,* 183-189.
2)Johnson, J. A.; Lu, Y. Y.; Burts, A. O.; Xia, Y.; Durrell, A. C.; Tirrell, D. A; Grubbs, R. H. Drug-Loaded, Bivalent-Bottle-Brush Polymers by Graft-through ROMP. *Macromolecules* **2010**, *43*, 10326–10335.

Brush Polymers

Synthesis of PBBs can be done using three different approaches

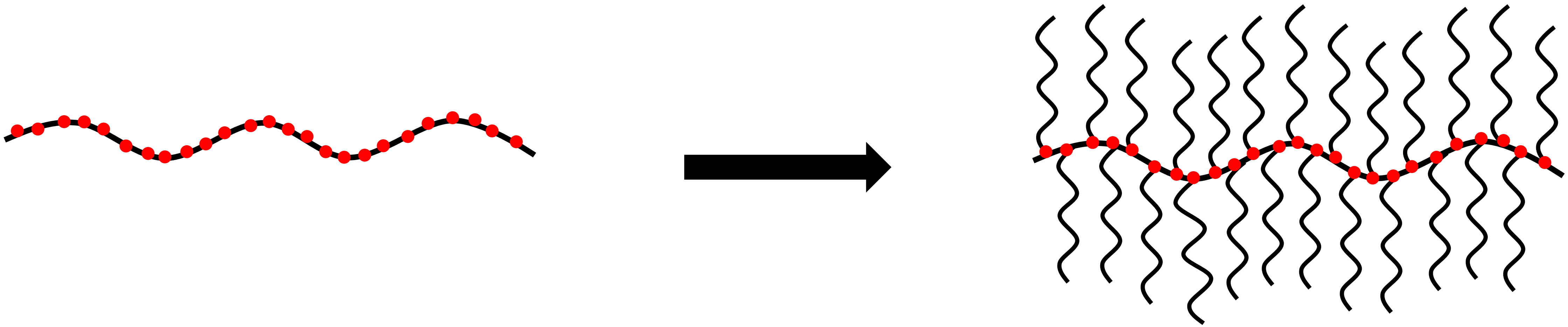
- Grafting through
  - Involves the synthesis of macromonomers
  - Pro:100% side chain attachment, high grafting density
  - Con: May be hard to obtain a high degree of polymerization



Brush Polymers

Grafting from

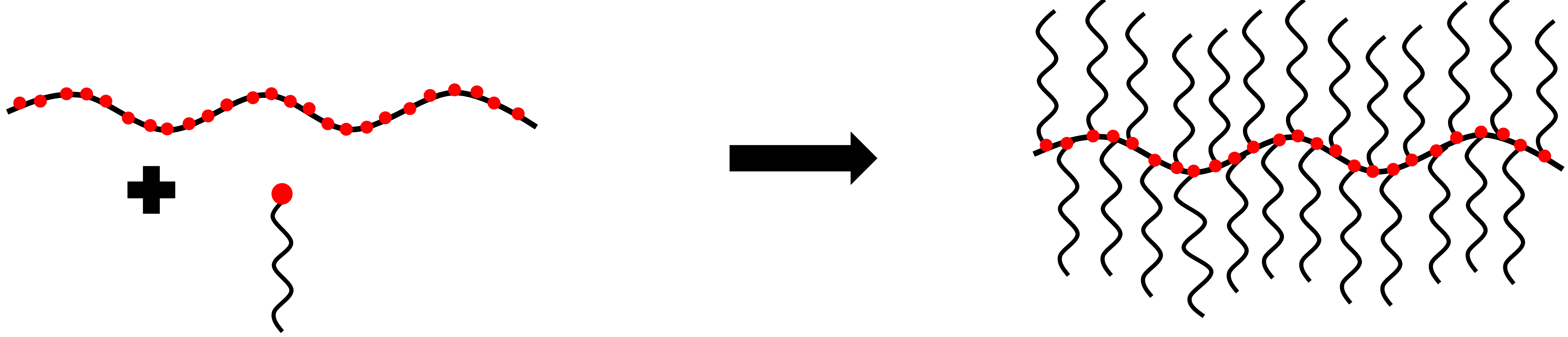
- Involves the synthesis of a macroinitiator from which the side chains can be grown from
- Pro: Large degree of polymerization possible
- Con: Side chain length can vary



Brush Polymers

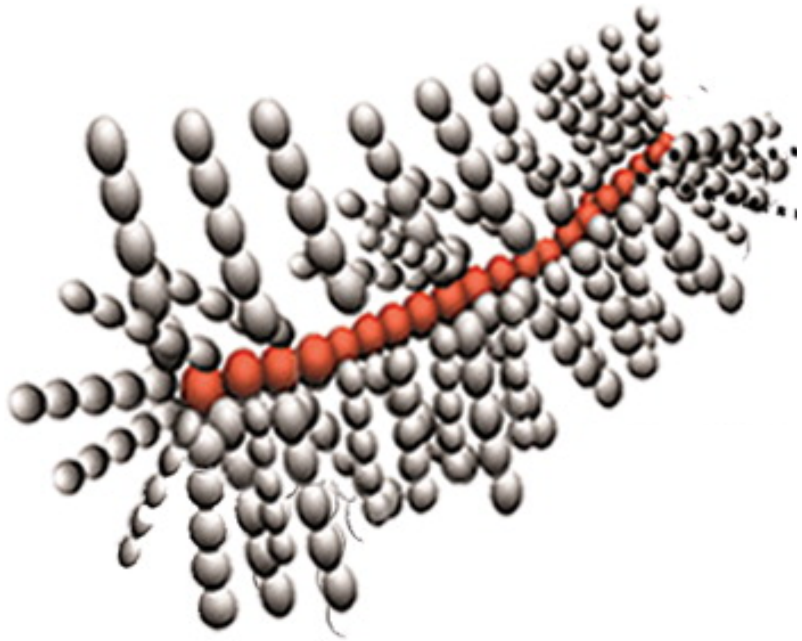
Grafting to

- Involves the synthesis of a polymer with side chains that can be coupled to another polymer
- Pro: Polymer backbone and side chains can be synthesized separately and with a large degree of polymerization
- Con: Requires a coupling reaction, can result in low and uneven grafting. Challenging if the polymers being coupled are bulky.

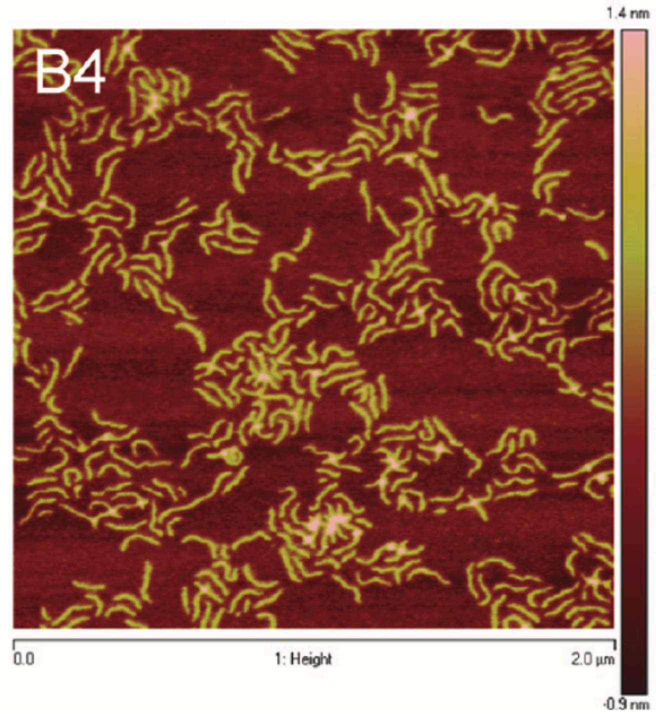


Brush Polymers in 3D Versus 2D

1)



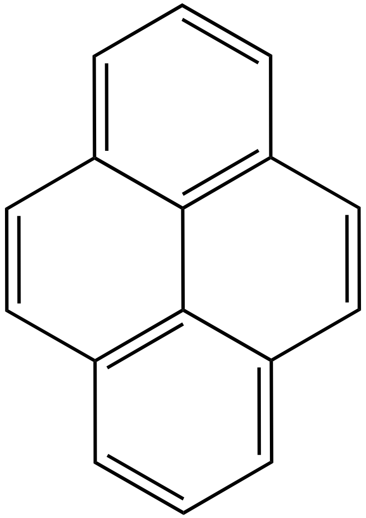
2)



1) Fouz, M. F.; Mukumoto, K.; Averick, S.; Molinar, O.; McCartney, B. M.; Matyjaszewski, K. Armitage, B. A.; Das, S. R. Bright fluorescent nanotags from bottlebrush polymers with DNA-tipped bristles. *ACS cent. sci.* **2015**, *1*, 431-438.
2) Nese, A.; Li, Y.; Averick, S.; Kwak, Y.; Konkolewicz, D.; Sheiko, S. S.; Matyjaszewski, K. Synthesis of Amphiphilic Poly(N-vinylpyrrolidone)-b-poly(vinyl acetate) Molecular Bottlebrushes. *ACS Macro Lett*. **2012**, *1*, 227-231.

Fluorescence

Fluorescence requires that a chromophore be covalently attached to the macromolecule being probed.



Pyrene was chosen because of its interesting characteristics:

- High molar extinction coefficient
- High quantum yield
- Excimer formation *

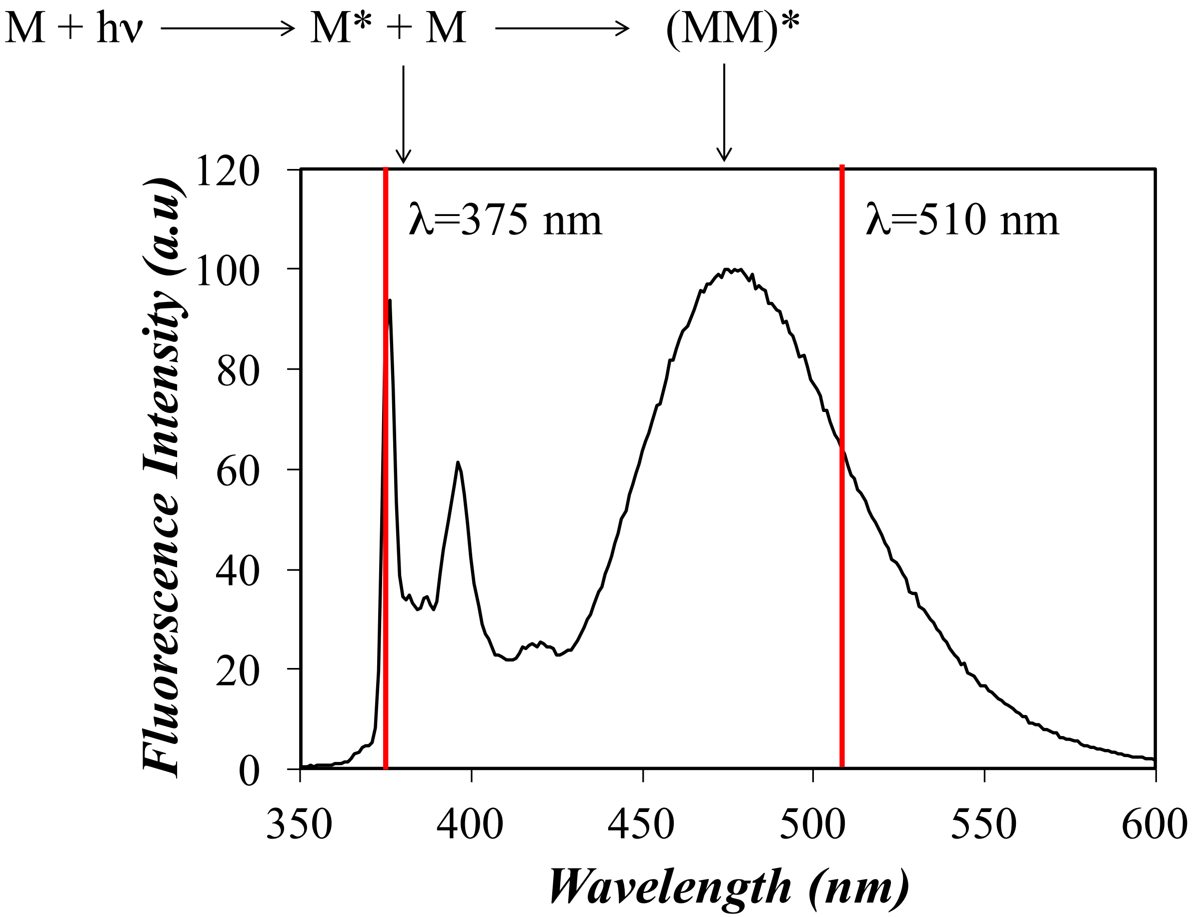
Fluorescence – Excimer Formation

$$M + h\nu \longrightarrow M^* + M \xrightarrow{\langle k \rangle} (MM)^*$$

$$M^* + M \;\downarrow\; \tau_M^{-1} \qquad\qquad (MM)^* \;\downarrow\; \tau_E^{-1}$$

M^* = Excited pyrene
M = Ground state pyrene monomer
$(MM)^*$ = Pyrene excimer
$\langle k \rangle$ = average rate constant of excimer formation

Steady-State (SS) Fluorescence

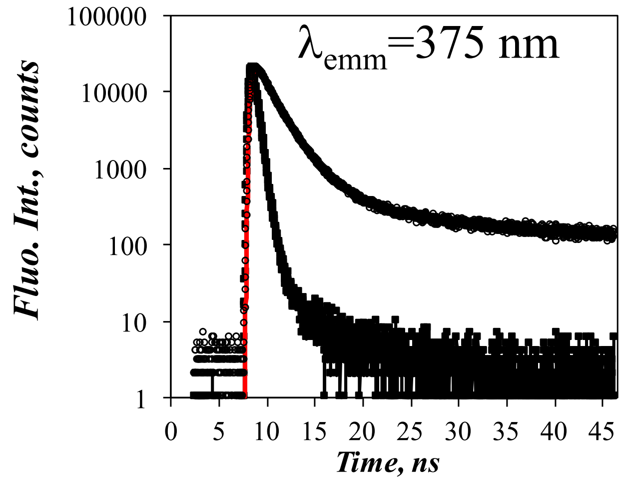


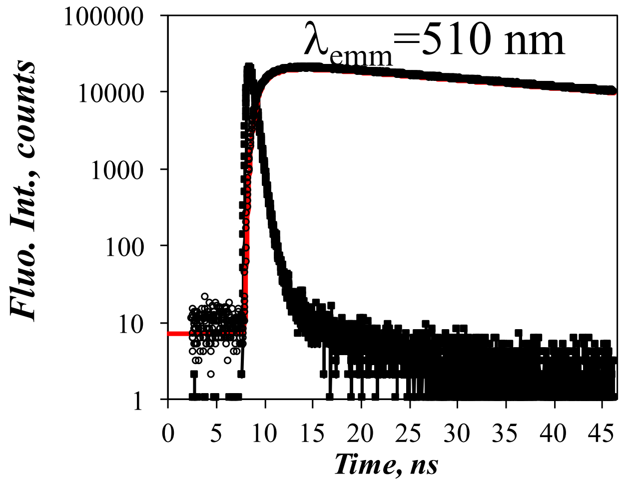
SS fluorescence measures the intensity of the monomer and excimer emission.

The monomer emission produces several fluorescence peaks between 375 nm and 410 nm.

Excimer emission produces a broad band which is centered around 480 nm.

Time Resolved (TR) Fluorescence





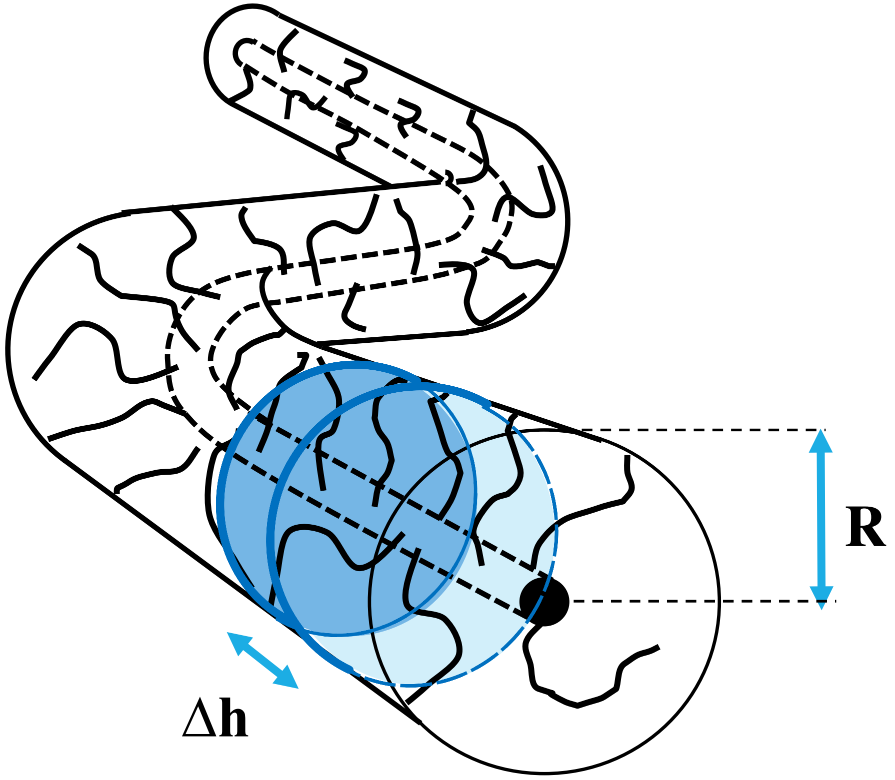
Monomer and excimer decays acquired at 344 nm.

Fluorescence of monomer monitored as a function of time at 375 nm.
Immediate decay of the monomer is seen.

Fluorescence of excimer monitored as a function of time at 510 nm.
Rise time is seen because of the time required for an excited pyrene to encounter a ground state pyrene.

$$\langle k \rangle = \mathrm{k_{diff}[Py]_{loc}}$$

Brush Polymers



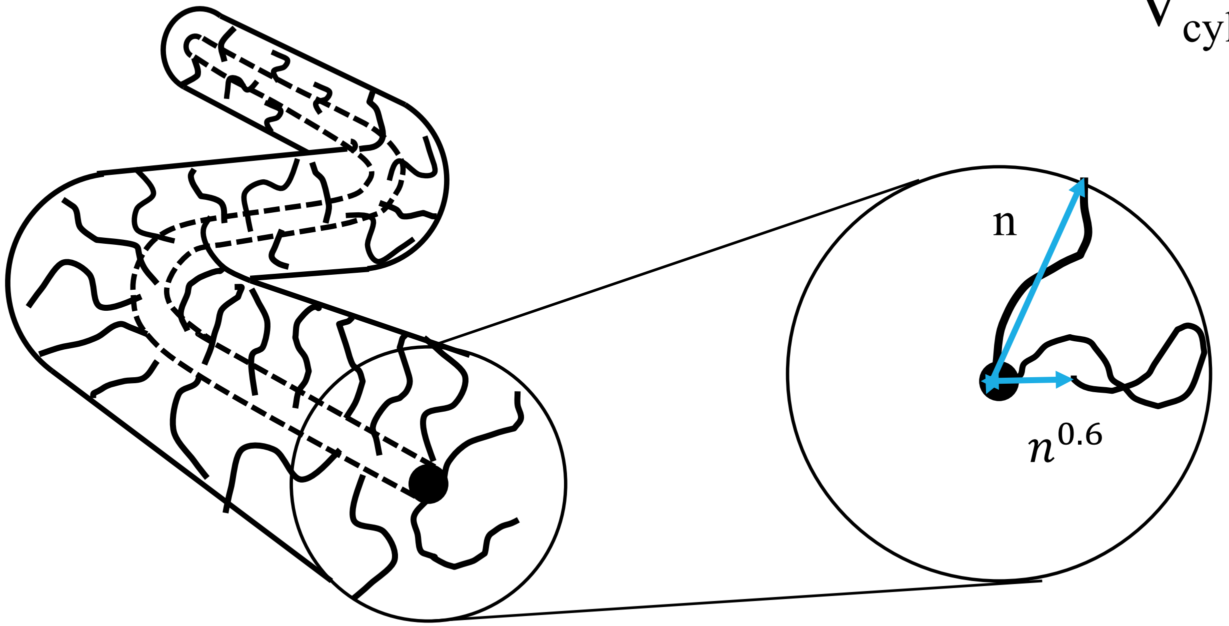
$$\langle k \rangle = k_{diff}[Py]_{loc}$$

$V_{cylinder}=\pi R^2 N\Delta h$ $V_{cylinder}/monomer=\pi R^2\Delta h$

$$[Py]_{loc} = \frac{1}{\pi R^2 \Delta h}$$

$$\langle k \rangle = k_{diff}[Py]_{loc} \propto \frac{1}{R^2}$$

Brush Polymers



$V_{cylinder} = \pi R^2 N \Delta h$ $V_{cylinder}/monomer = \pi R^2 \Delta h$

$$[Py]_{loc} = \frac{1}{\pi R^2 \Delta h}$$ $$R = n^{\alpha} l$$

$\alpha = 1$ For an extended conformation

OR

$\alpha = 0.6$ For a random coil in a good solvent

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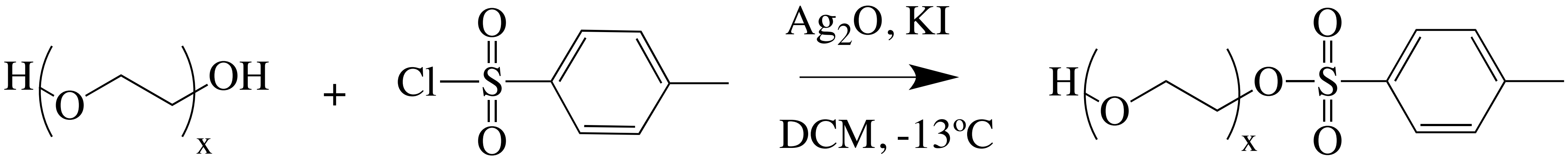
Results

1)



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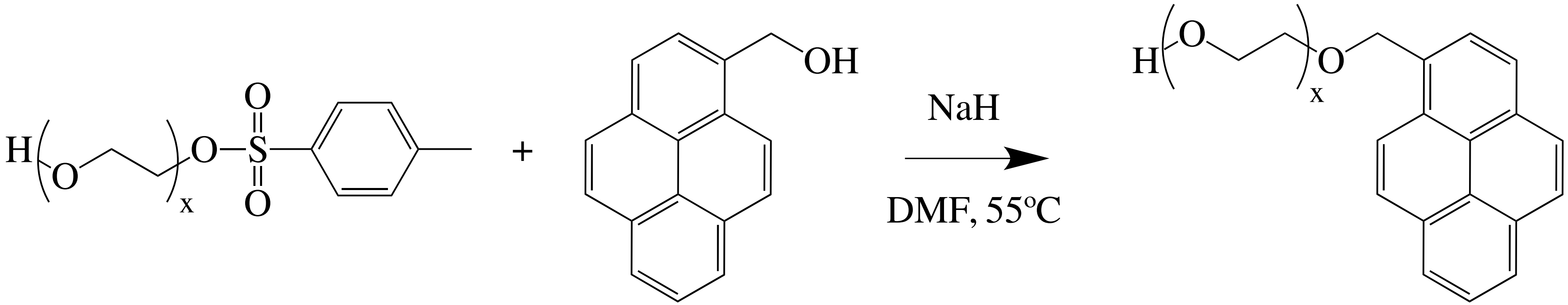

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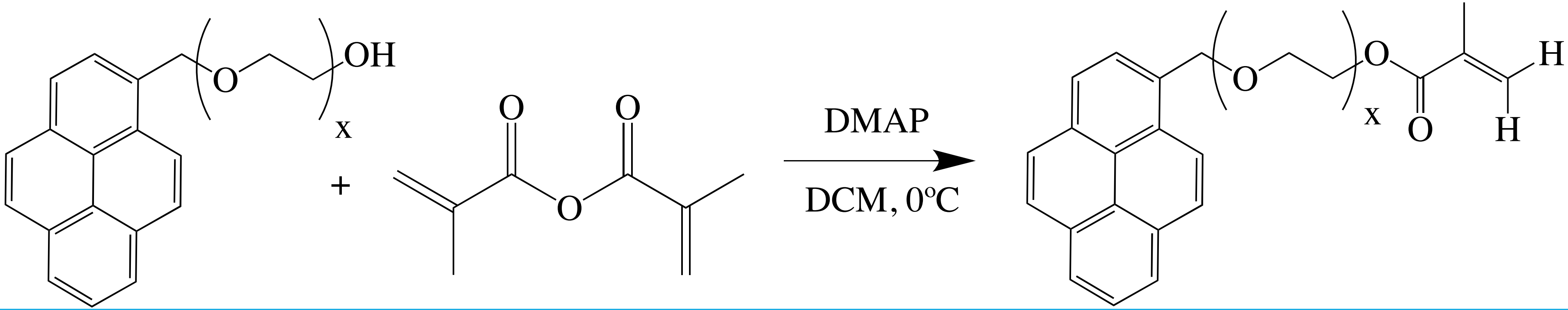
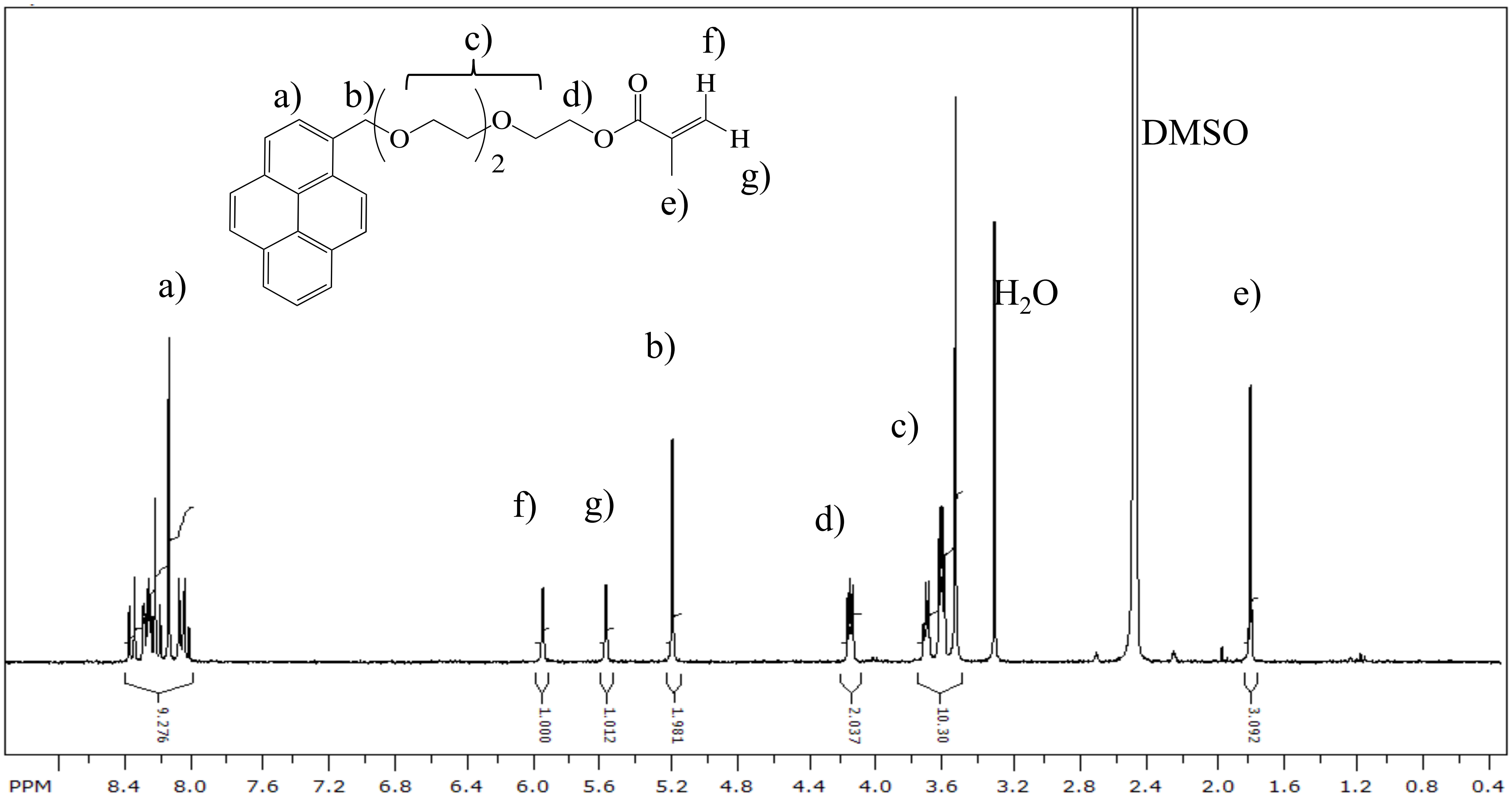
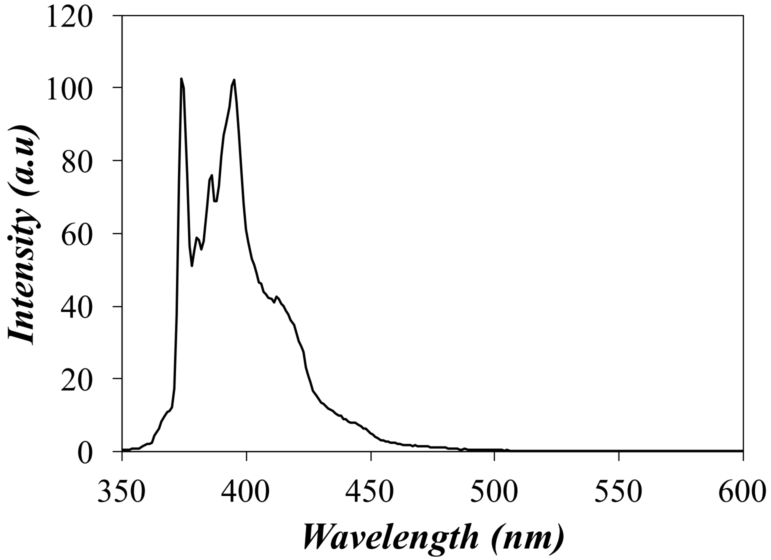


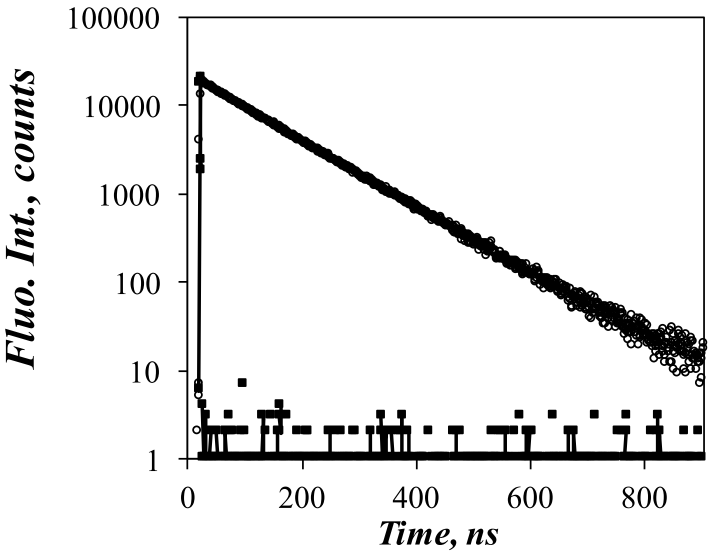
Monomers



a)
b)
c)
d)
e)
f)
g)
O
H
2
DMSO
H_2O
9.276
1.000
1.012
1.981
2.037
10.30
3.092
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4

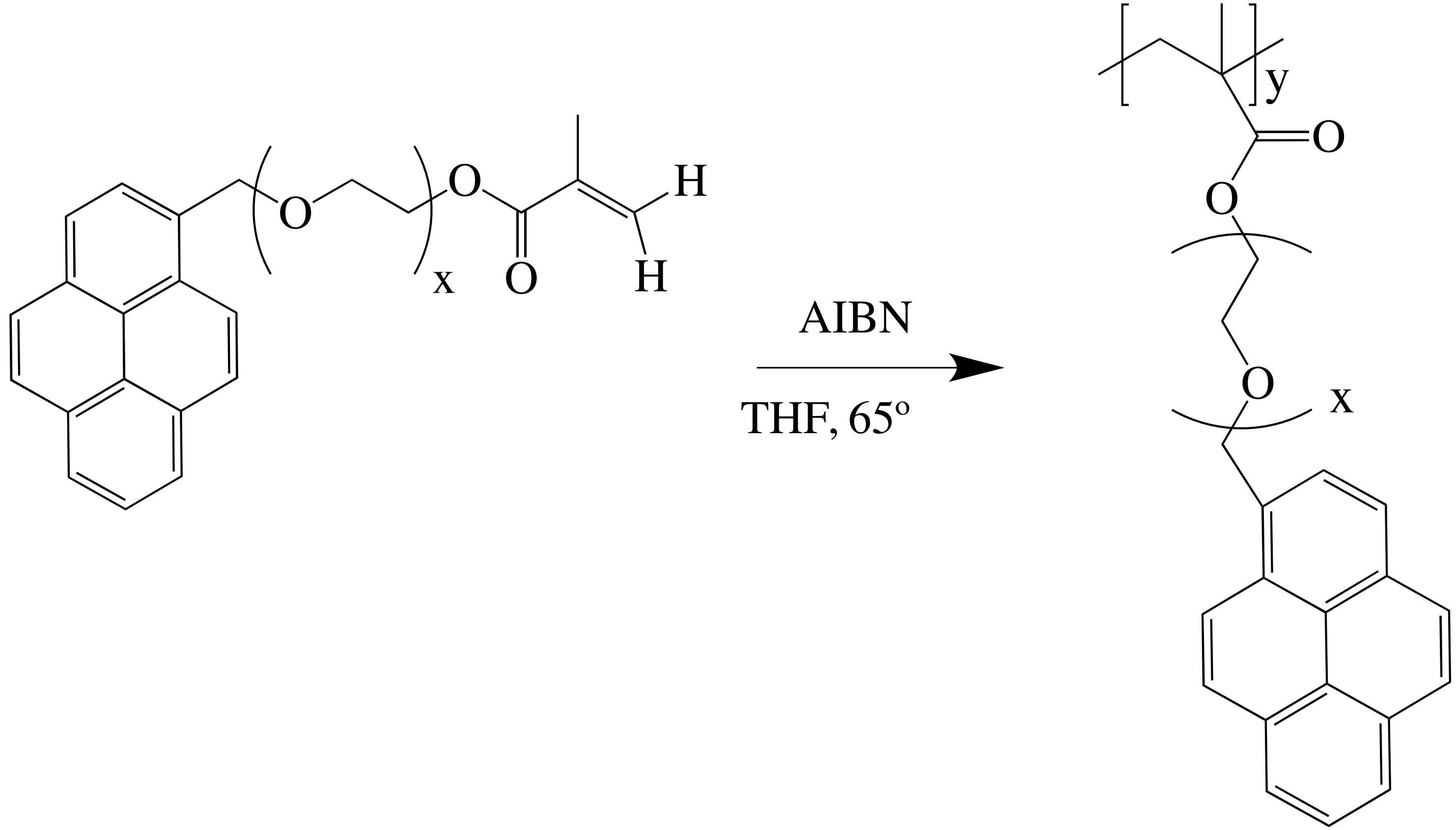
Monomers



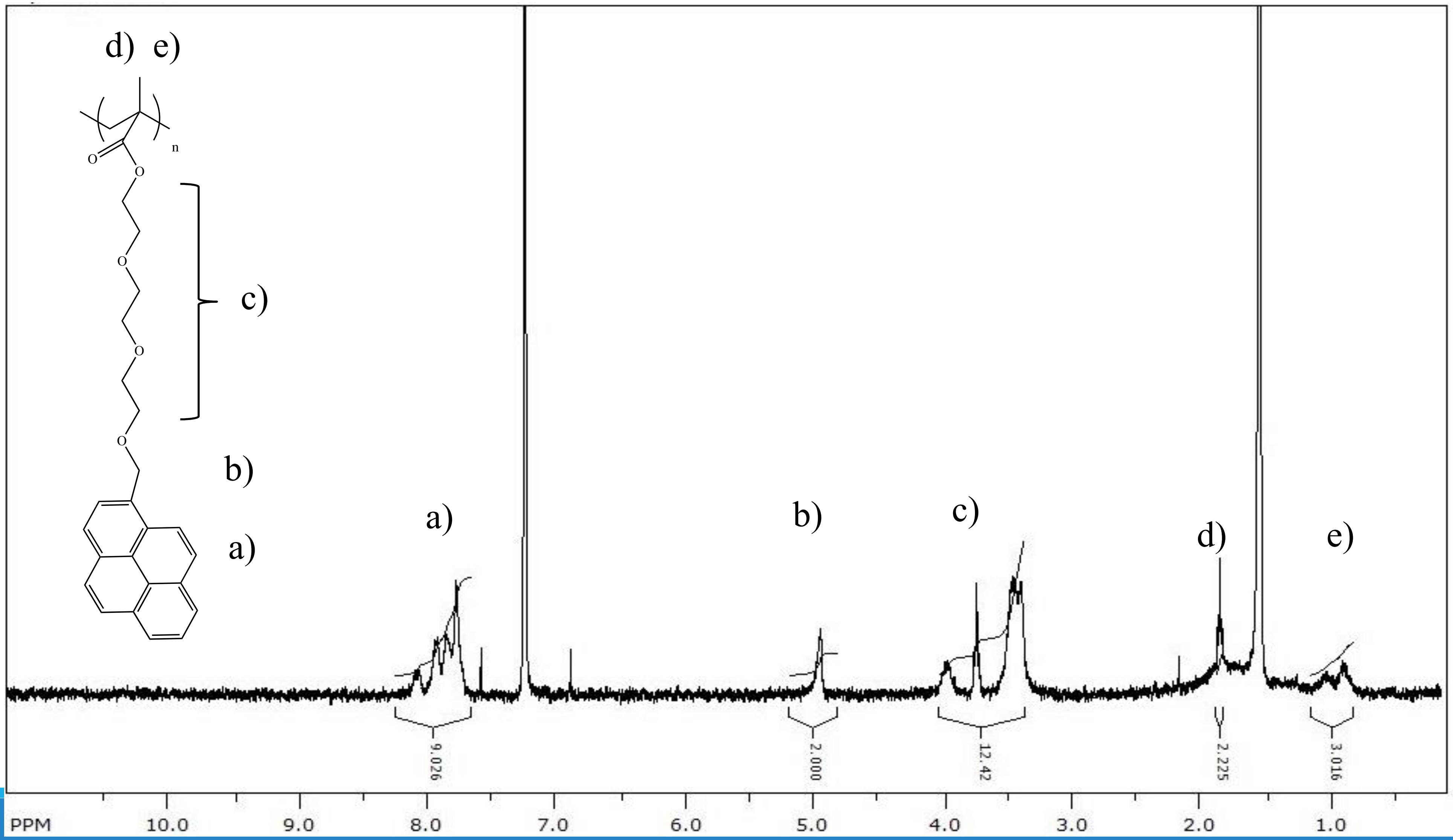


Monomer	Lifetime in THF (ns)	Contribution to decay
Py-EG_3-MA	280	0.98
Py-EG_5-MA	280	0.96
Py-EG_8-MA	280	0.97
Py-EG_{12}-MA	280	0.96

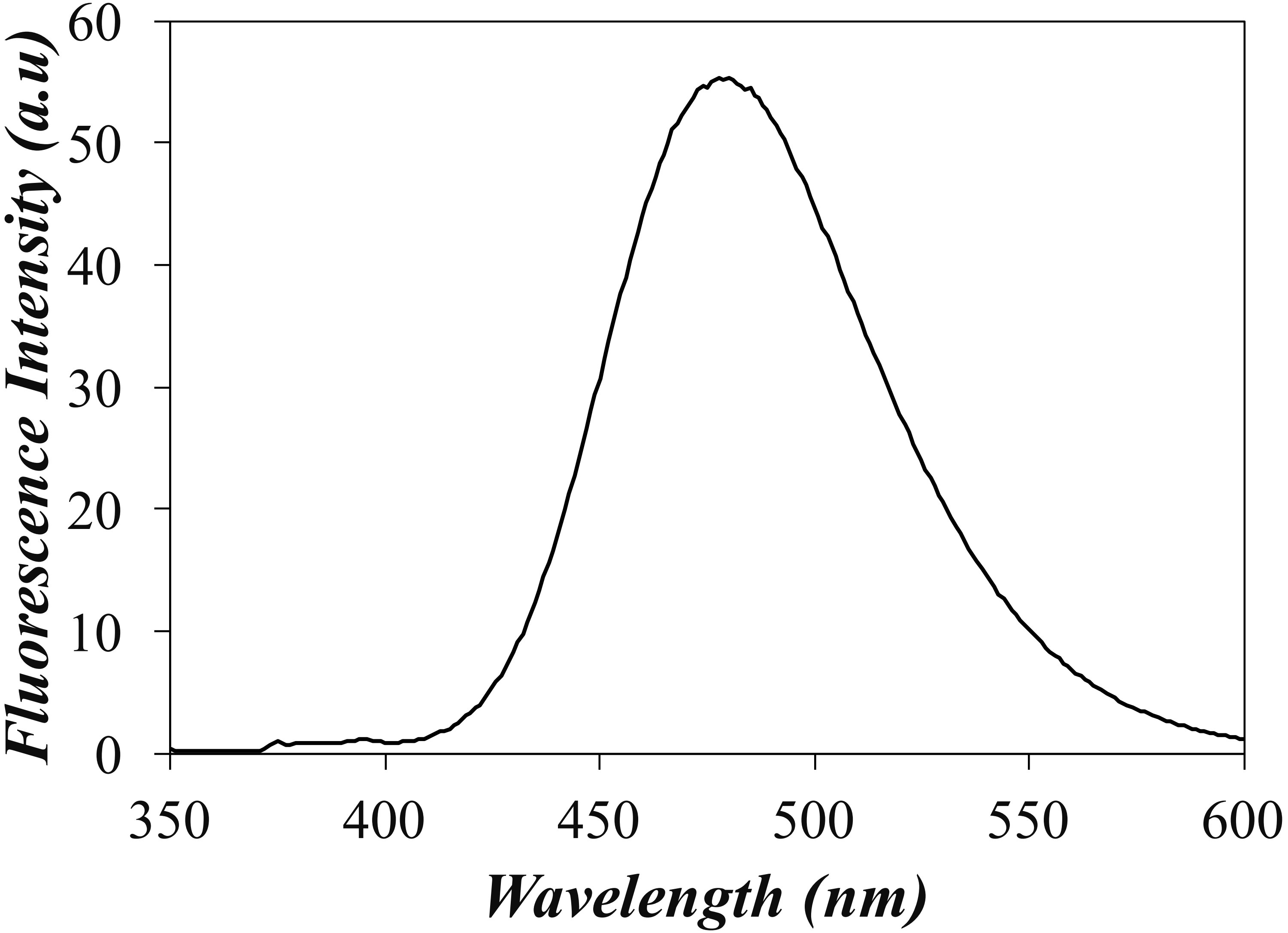
Polymers



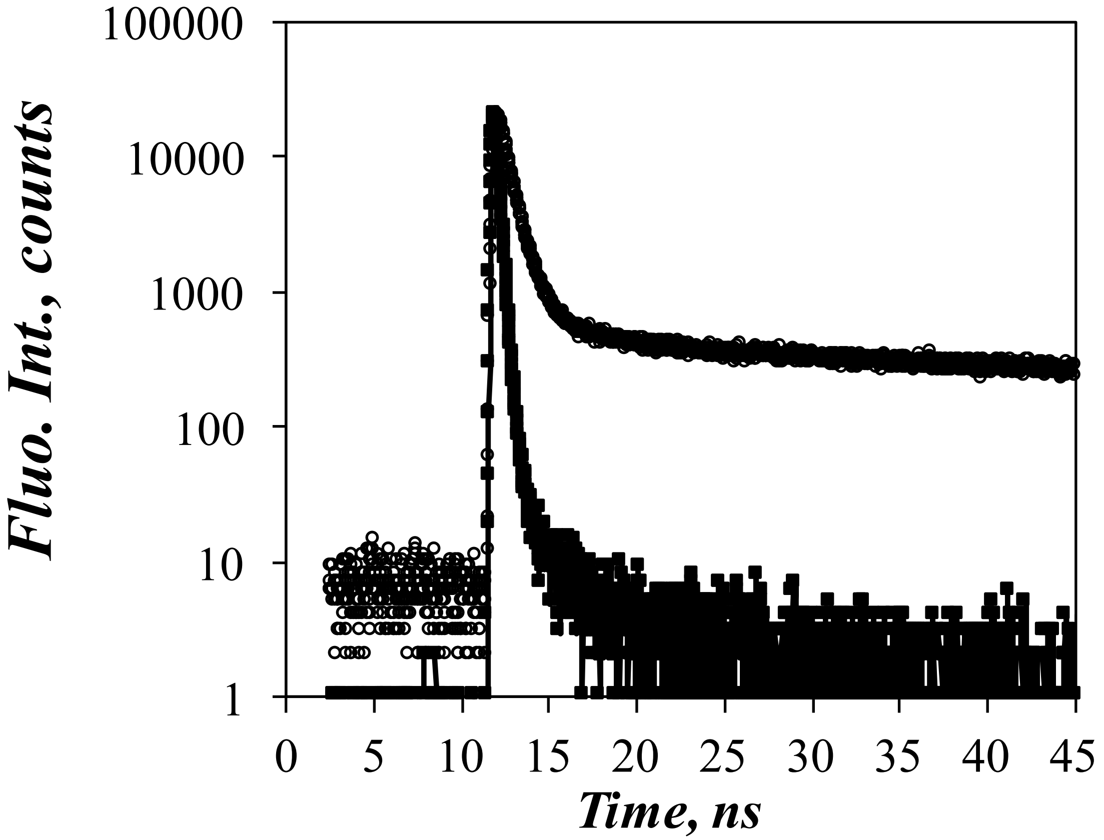
Polymers – poly($PyEG_3MA$)

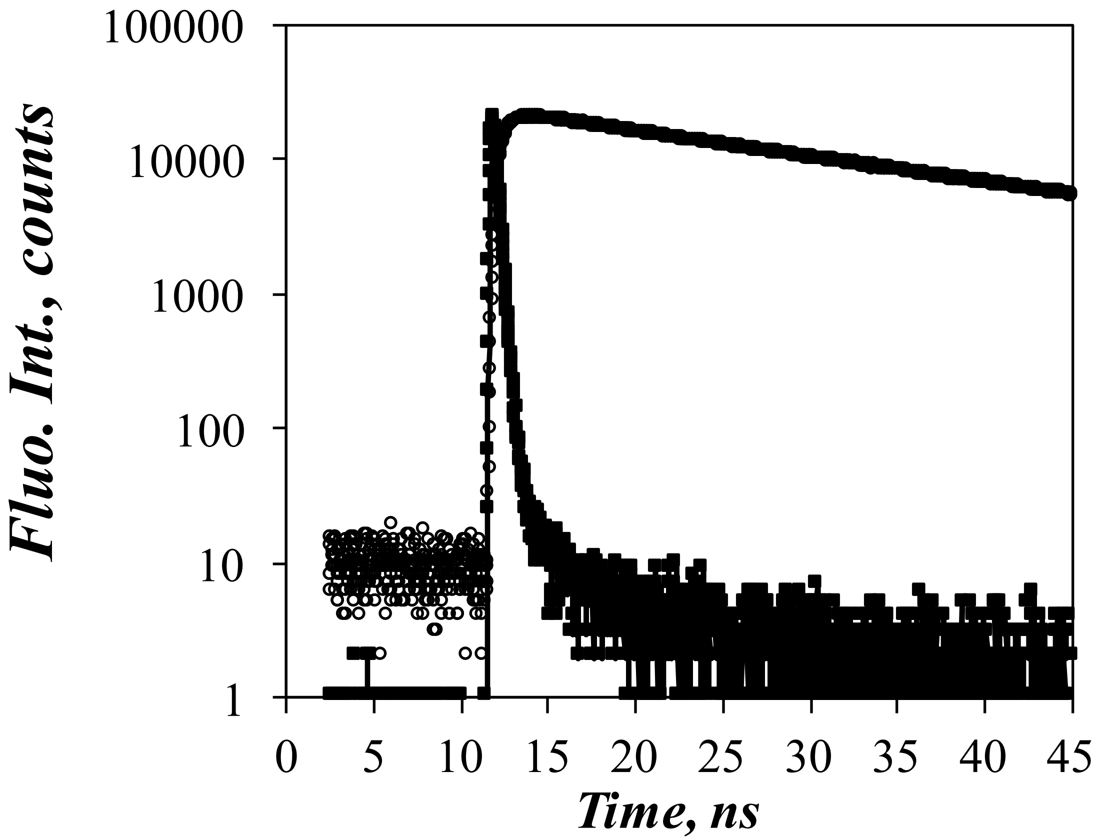


Polymers- poly($PyEG_3MA$)

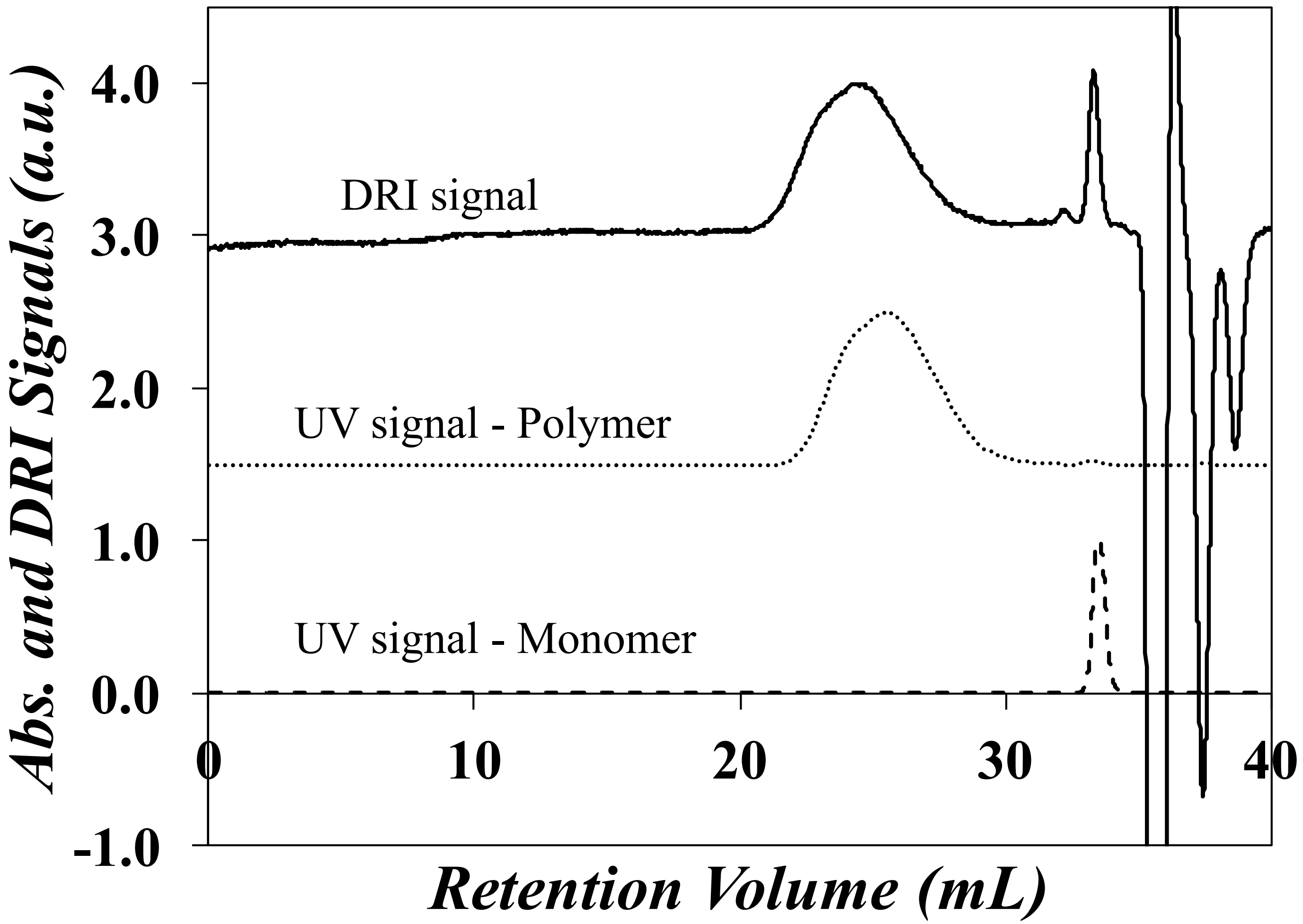


Polymers- poly($PyEG_3MA$)





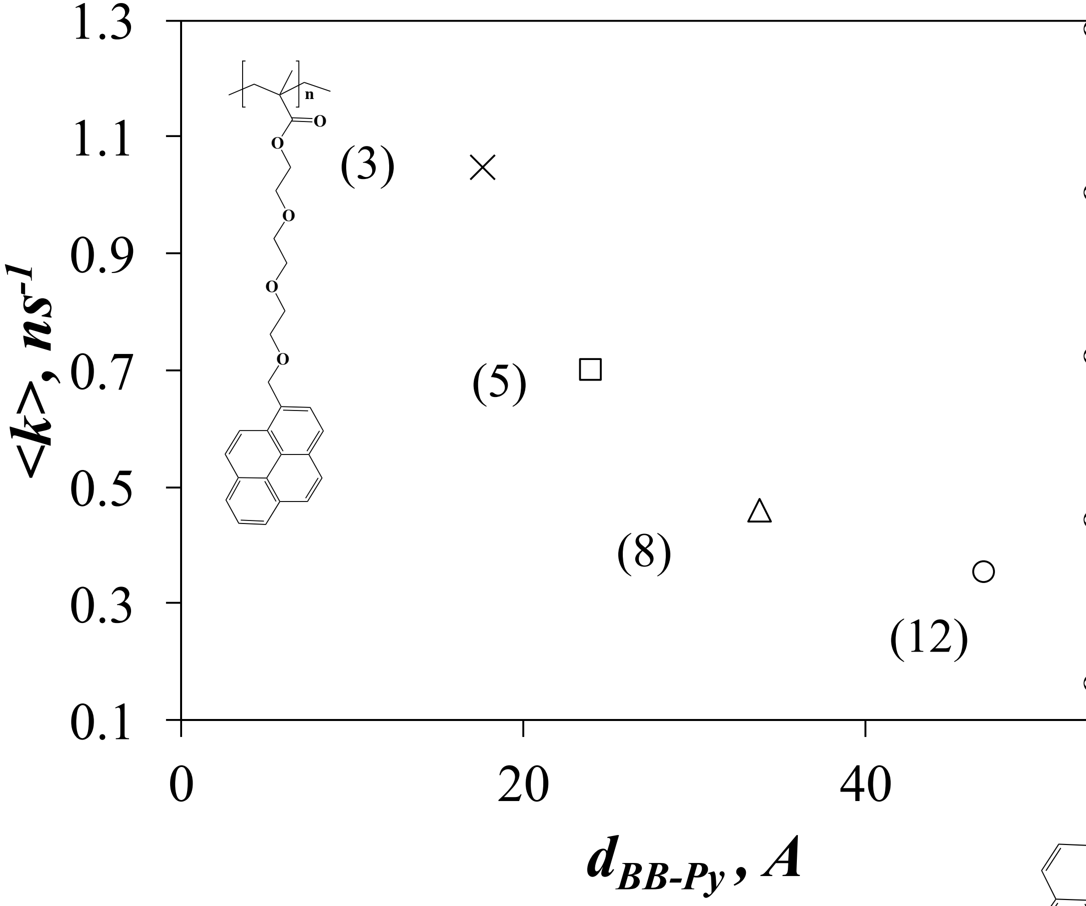
Polymers- GPC poly(PyEG$_5$MA) P2

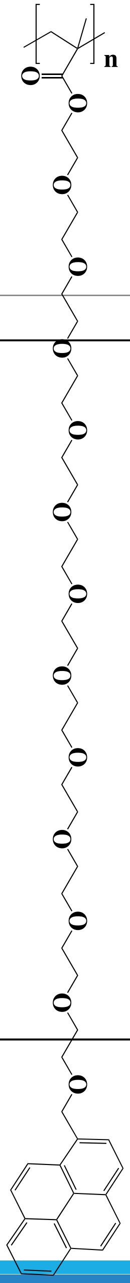


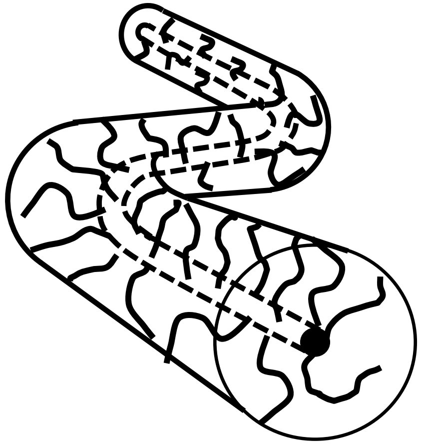
Polymers

Polymer	**M_n (kg/mol)**	**Degree of Polymerization**	**PDI**	**<k> (ns^{-1})**
Poly($PyEG_3MA$)	80	186	1.5	1.05
Poly($PyEG_5MA$)	61	117	1.5	0.68
Poly($PyEG_5MA$)	397	463	1.5	0.66
Poly($PyEG_8MA$)	51	77	1.9	0.46
Poly($PyEG_{12}MA$)	---	---	---	0.35

Polymers



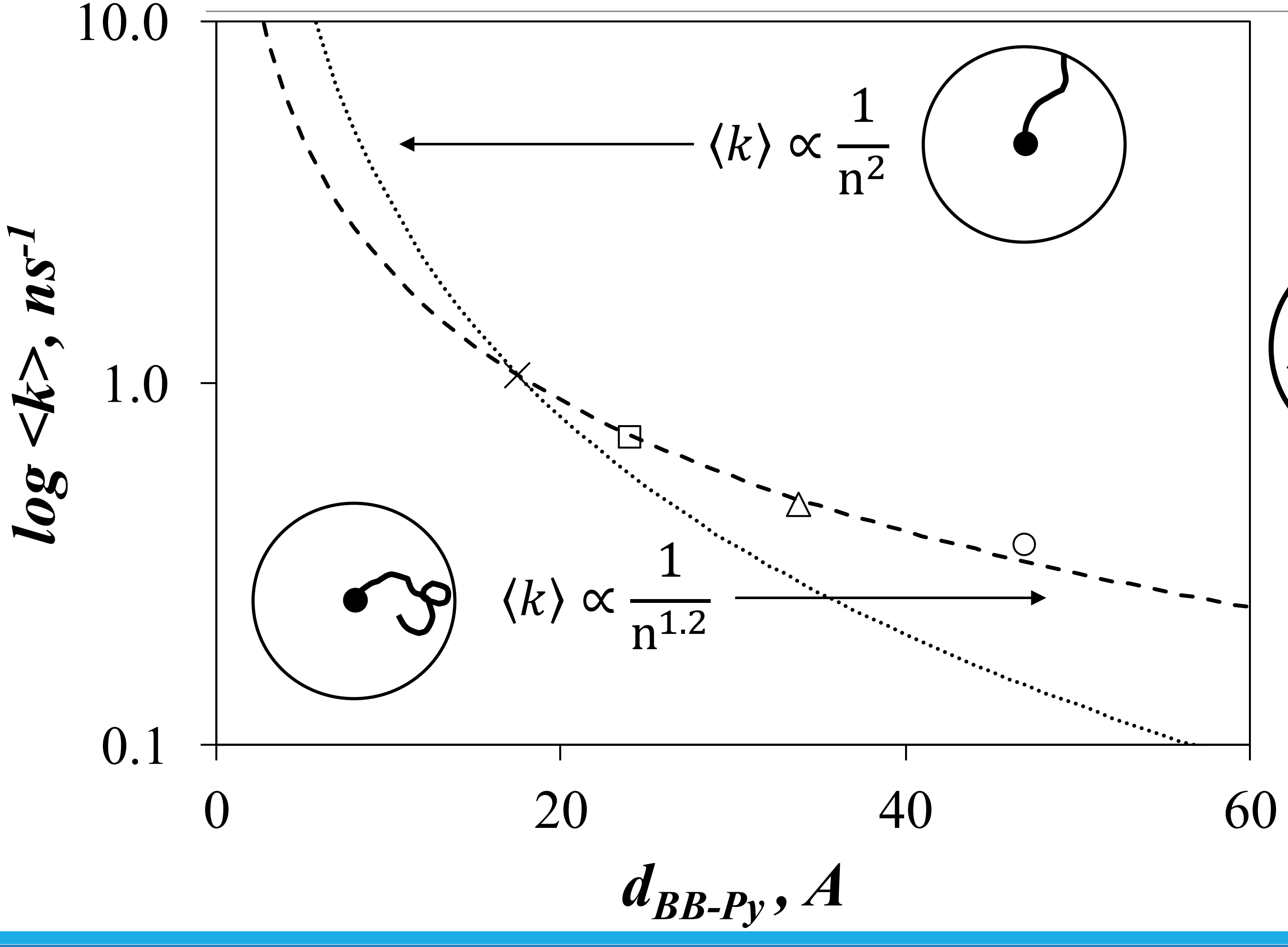


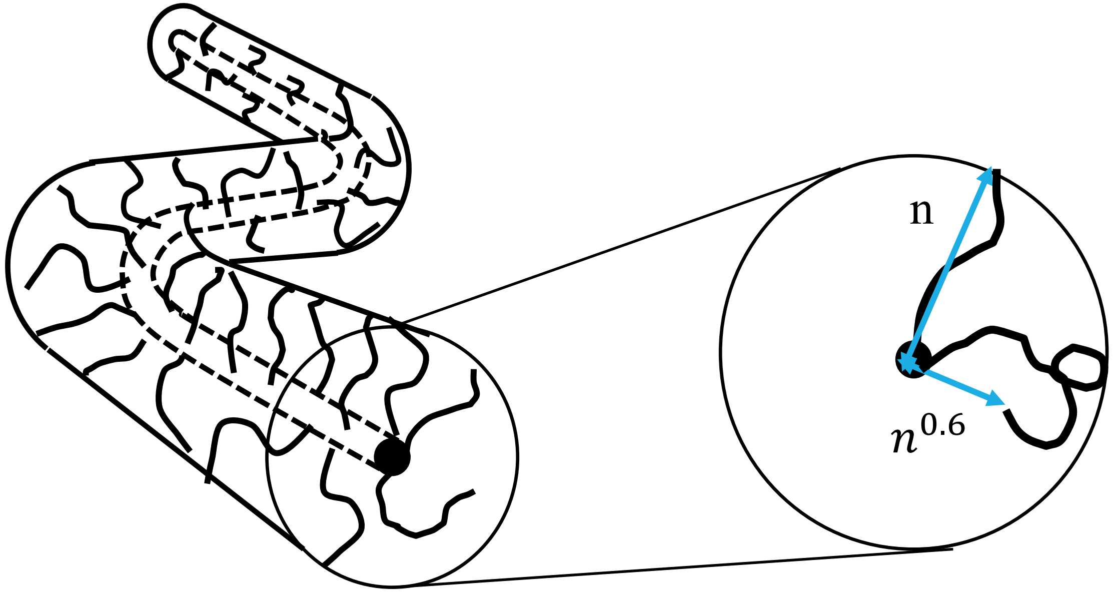


$$[\mathrm{Py}]_{\mathrm{loc}} = \frac{1}{\pi R^2 \Delta h}$$

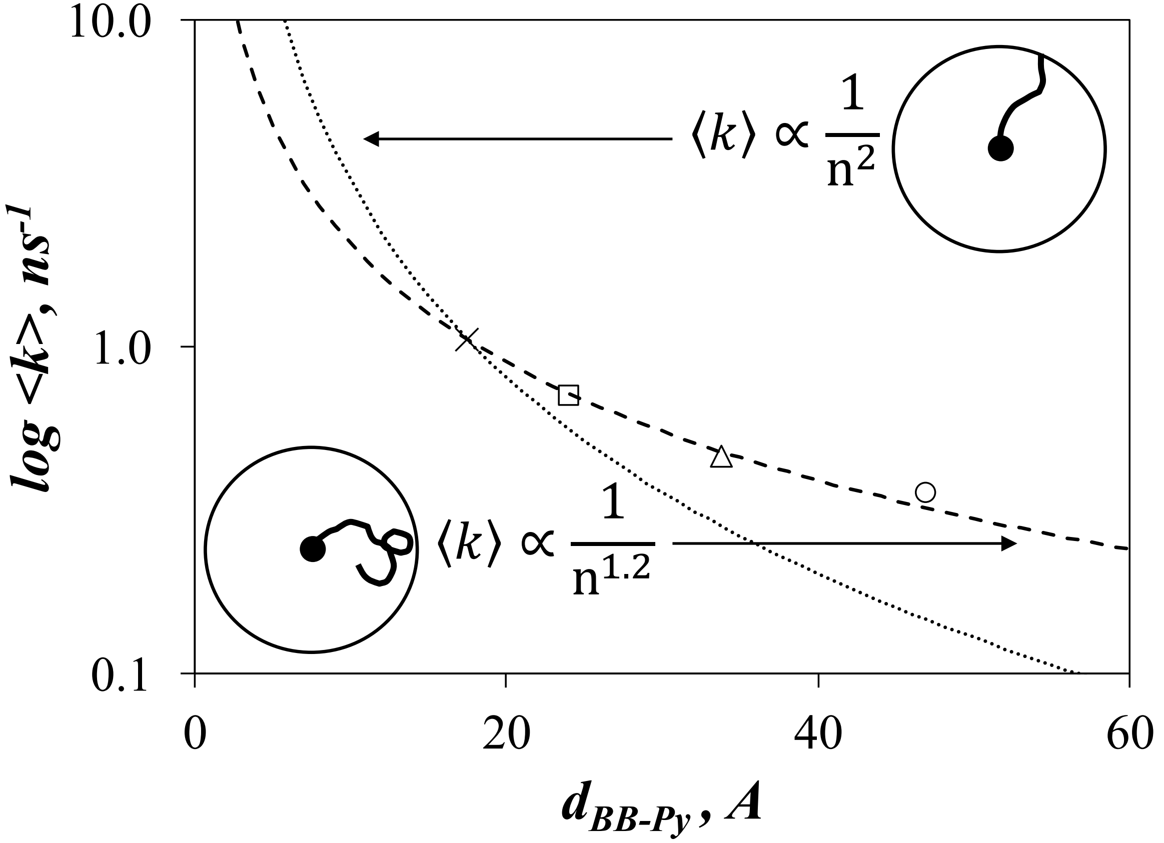
$$\langle k \rangle = k_{diff} \times [Py]_{loc}$$

Polymers

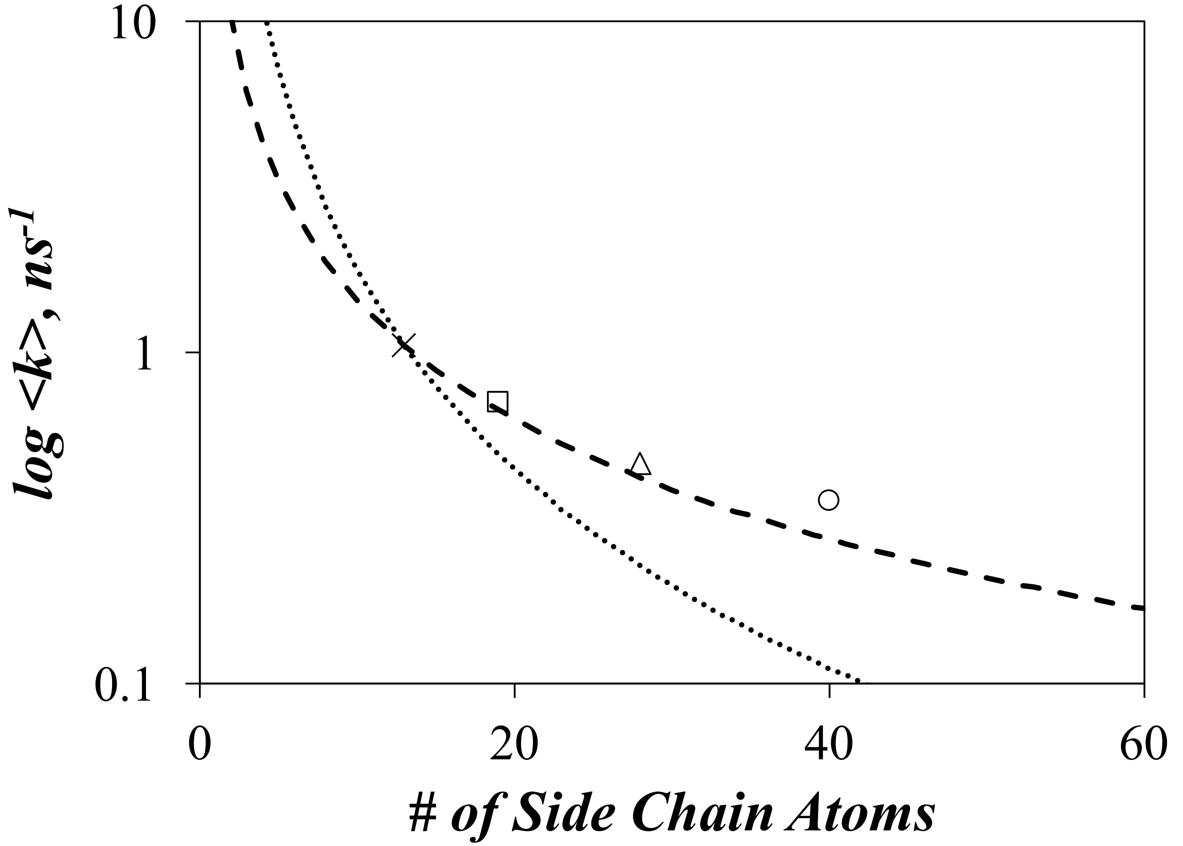




Polymers



10.0
1.0
0.1
0
20
40
60
log <k>, ns-1
d BB-Py , A
⟨k⟩ ∝ 1/n2
⟨k⟩ ∝ 1/n1.2



10
1
0.1
0
20
40
60
log <k>, ns-1
# of Side Chain Atoms

Conclusions

- The side chains of a brush polymer which contain 3, 5, 8, and 12 ethylene glycol units will adopt a random coil conformation in THF.

Future Work

- Characterize my Poly($PyEG_{12}MA$) polymer using GPC.
- Use a 400 g/mol and 1000 g/mol PEG polymer as my side chain. Then compare $<k>$ to the values obtained for my PEGMA polymers with monodispersed side chains.
- Investigate effect of solvent polarity on α.

I would like to thank:

Jean Duhamel
Mario Gauthier
Xiaosong Wang
Michael Tam
Everyone in the Duhamel and Gauthier labs