

Effect of Side Chain Length on the Internal Dynamics of Polymethacrylates in Solution

Shiva Farhangi, Henning Weiss, Jean Duhamel,
IPR Symposium, University of Waterloo, ON N2L 3G1, Canada

Introduction

The dynamics of polymer chains in solution are often invoked to rationalize the role of polymers in a number of phenomena such as the shear-thickening or thinning of solutions of viscosity modifiers or the folding of proteins in aqueous solution. Consequently, techniques capable of characterizing polymer chain dynamics in solution have attracted strong scientific interest.¹ To date, the procedure most applied and trusted to characterize polymer chain dynamics in solution consists in labeling the two ends of a linear chain with a dye and its quencher and monitoring how the rate constant of end-to-end cyclization (k_{cy}) changes with the nature of the polymer backbone. This procedure introduced close to 40 years ago by Zachariasse² to characterize the cyclization of pyrene end-labeled alkyl chains models was quickly applied to polymers by first Perico and Cunniberti³ followed by Winnik⁴. One major issue with this procedure is its limitation to short and monodisperse chains consisting of less than 100 monomers. For chains longer than 100 monomers, too few end-to-end cyclization (EEC) events take place to provide a reliable measurement of k_{cy} . In essence, the characterization of polymer chain dynamics is typically conducted with fluorescently end-labeled oligomers. This report is the first example in the literature where the polymer chain dynamics (PCD) of actual polymers are being compared as a function of the polymer chemical composition. The study of these polymers having large M_n values in the 170,000-810,000 $\text{g}\cdot\text{mol}^{-1}$ range was accomplished by labeling these high molecular weight samples randomly. A series of fluorescently labeled vinyl polymers bearing a C1-C18 side-chain (namely poly(methyl methacrylate), poly(butyl methacrylate), poly(octyl methacrylate), poly(lauryl methacrylate), and poly(stearyl methacrylate)) were synthesized and their PCD was characterized by applying the Fluorescence Blob Model (FBM).⁵ The effect on PCD resulting from a modification to the polymer backbone was investigated by applying the same FBM-protocol to study a series of fluorescently labeled poly(methyl acrylate)s. The FBM takes advantage of the ability of the dye pyrene to form an excimer. Global FBM analysis of the pyrene monomer and excimer fluorescence decays yielded the blob size N_{blob} and the rate of pyrene excimer formation inside a blob from the product $k_{\text{blob}} \times N_{\text{blob}}$. In the future, the body of results generated in this study is expected to become a reference for other polymers dynamic studies including protein chain dynamics influenced by the bulkiness of different side-chains.

Methodology

Random copolymerization: Pyrene-labeled polymethacrylates were prepared by copolymerization of 1-pyrenebutyl methacrylate with methyl, butyl, octyl, lauryl, and stearyl methacrylate to yield Py-PC1MA, Py-PC4MA, Py-PC8MA, Py-PC12MA, and Py-PC18MA, respectively. Copolymerization of 1-pyrenebutyl acrylate with methyl acrylate yielded a series of pyrene-labeled poly(methyl acrylate)s. The stabilizer added to the unlabeled monomers purchased from Aldrich was removed by filtration through column filled with MEHQ inhibitor-remover beads. The copolymerization was carried out in an oil bath at 65 °C using AIBN as the initiator. To minimize composition drift during the copolymerization, the reaction was stopped at a conversion of 0.2 or less as determined by ¹H NMR. Once the desired conversion was achieved, the reaction vessel was placed on ice and the polymer was precipitated in methanol, re-dissolved in THF, and re-precipitated in methanol 5-7 times to remove unreacted 1-pyrenebutyl methacrylate monomer. The final yield was approximately 10% in each copolymerization.

Steady-state fluorescence measurements: Steady-state fluorescence spectra were acquired on a Photon Technology International LS-100 steady-state fluorometer with an Ushio UXL-75 Xenon lamp and a PTI 814 photomultiplier detection system. The spectra were obtained using the usual right angle geometry. The samples were dissolved in tetrahydrofuran (THF) and diluted down to an optical density of ~ 0.1 to prevent intermolecular excimer formation. The solutions were degassed for approx. 30 minutes by bubbling nitrogen. The solution was excited at 344 nm. The emission spectrum was acquired from 350 nm up to 600 nm. Figure 1 displays a typical steady-state fluorescence spectra. The fluorescence intensity of the monomer (I_M) and excimer (I_E) were obtained by integrating the fluorescence of the monomer from 372 to 378 nm and the excimer from 500 to 530 nm. The I_E/I_M ratios provide a qualitative measure of the ability of a given pyrene-labeled polymer to form excimer.

Time-resolved fluorescence measurements: The monomer and excimer fluorescence decays were acquired with an IBH Ltd. time-resolved fluorometer equipped with an IBH 340 nm NanoLED. The samples were prepared in the same manner as for steady-state fluorescence and they were excited at 344 nm. The monomer and excimer emission were detected at 375 nm and 510 nm, respectively.

Molecular weight determination: The analysis of the polymer properties was achieved by Gel Permeation Chromatography (GPC) with a Triple Detector (refraction index (RI), viscosity, light scattering) and a UV-detector. Analysis of the light scattering signal provides the absolute molecular weight of the polymers. An overview of the molecular weights distributions of the samples is shown in Table 1 in terms of M_n and PDI values.

Table. 1 Molecular weights and PDIs of six different copolymers.

Py-PC1A			Py-PC1MA			Py-PC4MA		
Pyrene Content	Mn	PDI	Pyrene Content	Mn	PDI	Pyrene Content	Mn	PDI
[mol %]	[g/mol]	[-]	[mol %]	[g/mol]	[-]	[mol %]	[g/mol]	[-]
0.3	265,000	1.38	0.3	134,000	1.70	0.3	174,000	1.93
2.6	236,000	1.40	1.3	130,000	1.42	1.1	272,000	1.99
2.6	313,000	1.40	2.7	200,000	1.33	2.2	296,000	1.44
3.0	173,000	1.42	4.0	135,000	1.60	3.0	197,000	1.39
5.0	138,000	2.08	5.3	206,000	1.70	3.6	264,000	1.68
6.2	145,000	1.38	5.6	170,000	1.55	5.3	275,000	1.97
6.7	870,000	2.40	7.3	176,000	1.80	7.2	416,000	1.76
Py-PC8MA			Py-PC12MA			Py-PC18MA		
Pyrene Content	Mn	PDI	Pyrene Content	Mn	PDI	Pyrene Content	Mn	PDI
[mol %]	[g/mol]	[-]	[mol %]	[g/mol]	[-]	[mol %]	[g/mol]	[-]
0.4	244,000	1.87	0.5	530,000	1.72	0.7	563,000	1.54
1.8	305,000	1.88	1.4	265,000	1.70	1.4	810,000	1.52
2.7	312,000	1.75	3.5	244,000	2.43	4.5	480,000	1.44
4.3	146,000	2.04	5.6	507,000	1.70	5.9	663,000	1.42
5.1	371,000	1.83	6.0	174,000	2.17	6.8	705,000	1.41
6.1	234,000	1.88	7.7	662,000	2.10	6.7	719,000	1.49
7.3	271,000	2.07	10.2	265,000	1.68	14.2	770,000	1.45

Results and Discussion

The steady-state fluorescence spectra acquired for a series of Py-PC12MA samples with different pyrene content ranging from 1-10 mol% are shown in Figure 1. The intensity was normalized at the monomer peak at 375 nm.

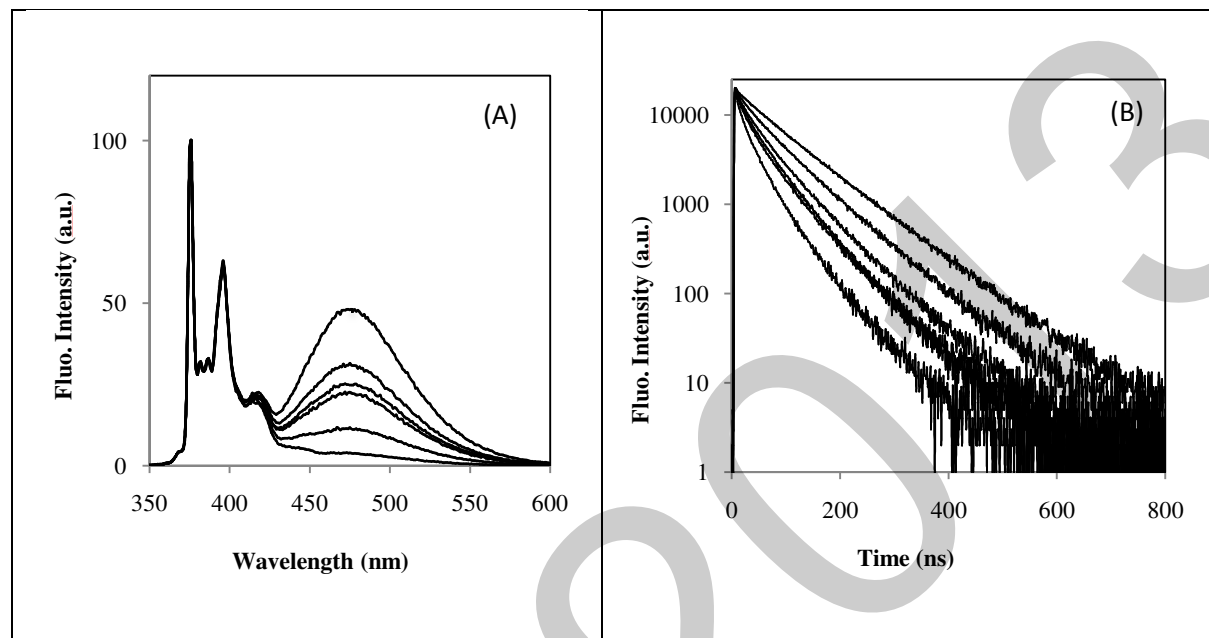


Fig. 1. A) Steady-state fluorescence spectra of Py-PC12MA in THF; Pyrene content decreased from top (10 mol%) to bottom (1 mol%). B) Time-resolved fluorescence decay of Py-PC12MA in THF. Pyrene content increased from bottom

Figure 1A depicts the fluorescence intensity of Py-PC12MA with a pyrene content ranging from 10.2 mol% to 1.4 mol% for the samples showing the largest to weakest excimer formation. The I_E/I_M ratios calculated from the fluorescence spectra were plotted as a function of pyrene content in Figure 2. It can be seen for all polymers that the I_E/I_M ratio increased with increasing pyrene content and decreasing side chain length. However, the increase in I_E/I_M was most pronounced for the polyacrylate series whose backbone is the least sterically hindered. These results indicate that pyrene excimer formation is affected by the size of the side-chain of the methacrylate monomer and the number of substituents of the vinyl monomer (methyl acrylate vs. methyl methacrylate).

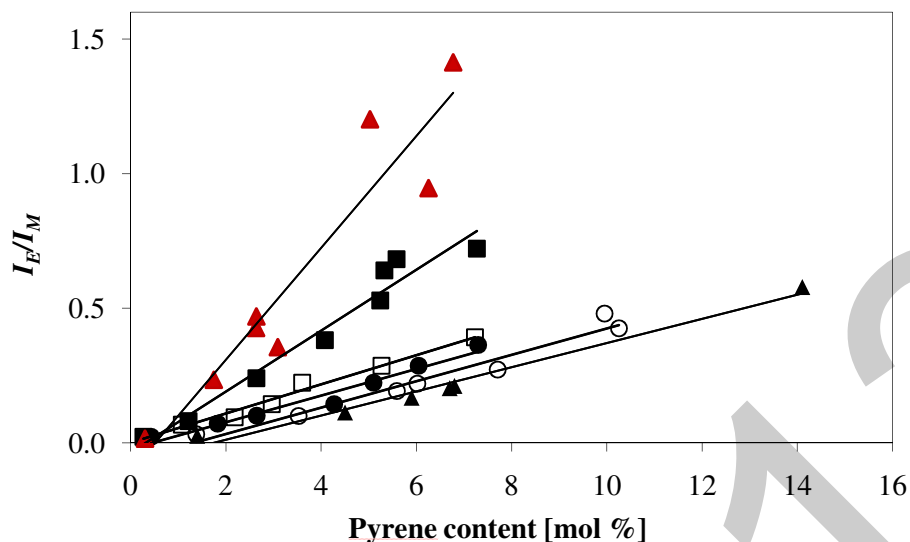


Fig. 2 I_E/I_M ratios for all polymers with increasing pyrene contents; \blacktriangle Py-PC1A, \blacksquare Py-PC1MA, \square Py-PC4MMA, \bullet Py-PC8MMA, \circ Py-PC12MMA, \blacktriangle Py-PC18MMA

While the information on chain dynamics retrieved from steady-state fluorescence remains qualitative, a quantitative description of polymer chain dynamics is afforded by the FBM analysis of the fluorescence decays. Global FBM analysis of the pyrene monomer and excimer fluorescence decays yielded the blob size N_{blob} and the rate of pyrene excimer formation inside a blob from the product $k_{\text{blob}} \times N_{\text{blob}}$ (Fig. 3 and 4).

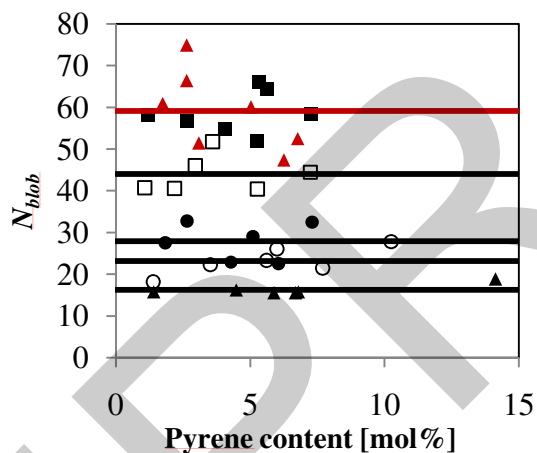


Fig. 3 N_{blob} values for the pyrene labeled copolymers; \blacktriangle Py-PC1A, \blacksquare Py-PC1MA, \square Py-PC4MMA, \bullet Py-PC8MMA, \circ Py-PC12MMA, \blacktriangle Py-PC18MMA

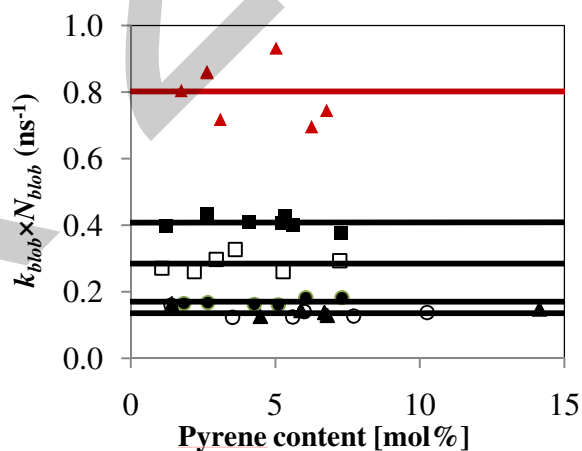


Fig. 4 $k_{\text{blob}} \times N_{\text{blob}}$ values for the pyrene labeled copolymers; \blacktriangle Py-PC1A, \blacksquare Py-PC1MA, \square Py-PC4MMA, \bullet Py-PC8MMA, \circ Py-PC12MMA, \blacktriangle Py-PC18MMA

For each series, both N_{blob} and $k_{\text{blob}} \times N_{\text{blob}}$ remained constant with experimental error with pyrene content, but their average value $\langle N_{\text{blob}} \rangle$ and $\langle k_{\text{blob}} \times N_{\text{blob}} \rangle$ decreased substantially with increasing side-chain length, demonstrating that an increase in bulkiness of the side-chain is associated with a pronounced decrease in chain mobility (Fig. 5 and 6). Within experimental error $\langle N_{\text{blob}} \rangle$ took the same value for Py-PC1A and Py-PC1MA. In contrast, $\langle k_{\text{blob}} \times N_{\text{blob}} \rangle$ was much larger for the Py-PC1A samples. Since the only structural difference between the Py-PC1MA and Py-PC1A samples is the lack

of a methyl group on the polyacrylate backbone, we can conclude that the presence of a methyl group hinders the chain dynamics drastically.

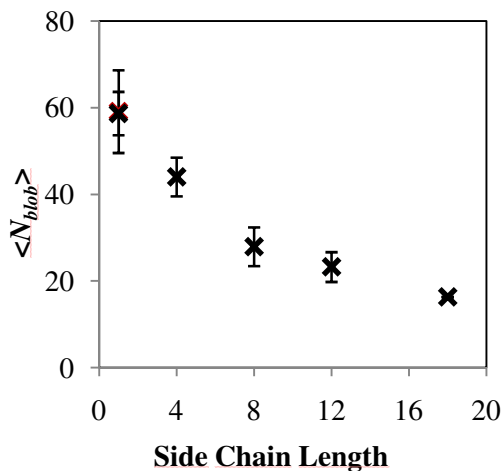


Fig. 3 $\langle N_{\text{blob}} \rangle$ values for pyrene labeled copolymers as a function of side-chain length. \times polymethacrylates, \times polyacrylate

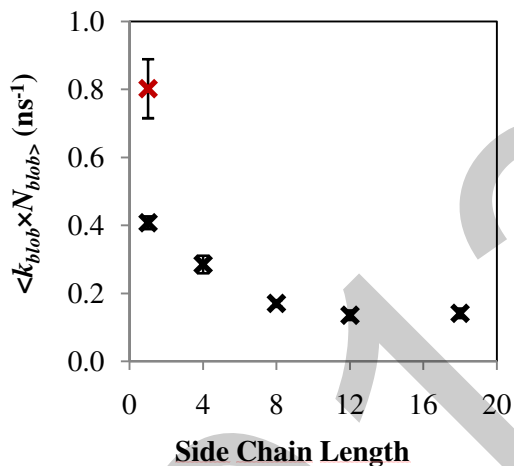


Fig. 4 $\langle k_{\text{blob}} \times N_{\text{blob}} \rangle$ values for pyrene labeled copolymers as a function of side-chain lengths; \times polymethacrylates, \times polyacrylate

References:

- [1] Duhamel, J. New Insights in the Study of Pyrene Excimer Fluorescence to Characterize Macromolecules and their Supramolecular Assemblies in Solution. *Langmuir* **2012**, *28*, 6527-6538.
- [2] Zachariasse, K.; Kühnle, W. Intramolecular Excimers with α,ω -Diarylalkanes. *Z. Phys. Chem. Neue Fol.* **1976**, *101*, 267-276.
- [3] Cuniberti, C.; Perico, A. Intramolecular Excimers and Microbrownian Motion of Flexible Polymer Molecules in Solution. *Eur. Polym. J.* **1977**, *13*, 369-374.
- [4] Winnik, M.A.; Redpath, T.; Richards, D.H. The Dynamics of End-to-End Cyclization in Polystyrene Probed by Pyrene Excimer Formation. *Macromolecules* **1980**, *13*, 328-335.
- [5] Duhamel, J. Polymer Chain Dynamics in Solution Probed with a Fluorescence Blob Model. *Acc. Chem. Res.* **2006**, *39*, 953-960.

Effect Of Side Chain Length On The Internal Dynamics Of Polymethacrylates In Solution

Presented by Shiva Farhangi

Supervised by: Dr. Jean Duhamel



IPR Symposium, May 8, 2013

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1. Basics

Motivation:

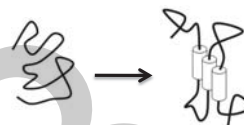
- The dynamics of polymer chains in solution play an important role in different polymeric systems

Examples:

- Viscosity modifiers in oil and aqueous solutions

- Protein folding in biological systems

→ properties extremely structure depending!

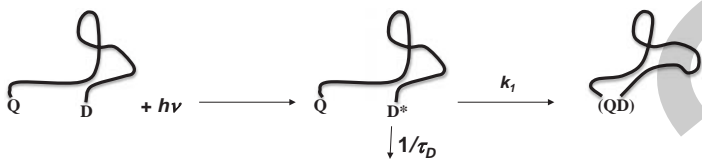


- The properties are influenced by the ability of the polymer backbone to move.

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1. Basics

-FDQ quenching



- Only the chain ends are being probed.
- Monodispersed samples only can be probed.
- Limited to short chains. k_{cy} decrease and no quenching can be observed while the chromophore remains excited.

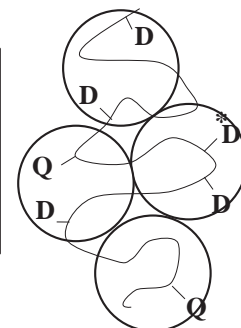
Winnik, M. A. End-to-End Cyclization of Polymer Chains. *Acc. Chem. Res.* 1985, 18, 73-79.

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1. Basics

✓ Hence Polymers is labelled randomly

- ❖ Dealing with different excimer formation rate constants
- ❖ Complicated data

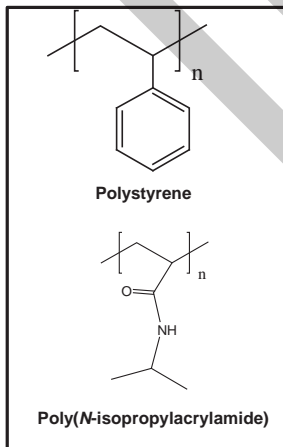


Solution to this problem was proposed in 1999 by introducing the Fluorescence Blob Model (FBM). FBM is a versatile and novel mathematical tool in polymer science which provide information about the internal chain dynamics of a number of polymers. The model is based upon the assumption that an excited dye can probe a finite volume in space, and this volume is referred to as a Blob.

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1. Basics

- Applicability of the FBM analysis



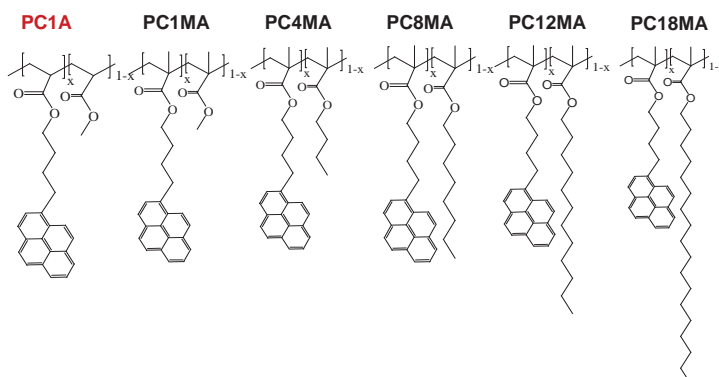
- Short monodisperse polymer of polystyrene (PS) were pyrene end-labelled and decays were acquired and fitted to Birks' scheme.
- PS randomly labelled with pyrene was synthesized and fitted in FBM.
- It was shown that the parameters describing the chain dynamic of PS show the same trends whether the labels were attached randomly or at the chain ends of a monodisperse polymer.
- The same conclusions were reached for PNIPAM.

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2. Sample Preparation

Poly(methacrylates) randomly labeled with pyrene;

Radical copolymerization: 1-Pyrenebutyl methacrylate + Monomer



2. Sample Preparation

✓NMR :

✓Determine the degree of conversion.

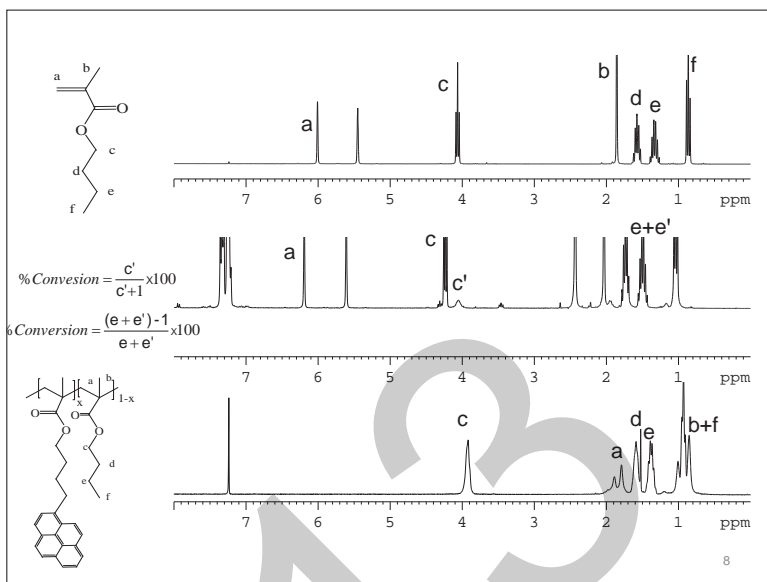
✓GPC:

✓ Check for unreacted pyrene monomer using UV-Vis absorption detector.
 ✓Determine molecular weight.

✓Absorption spectroscopy:

✓Pyrene content was determined for all polymers samples.

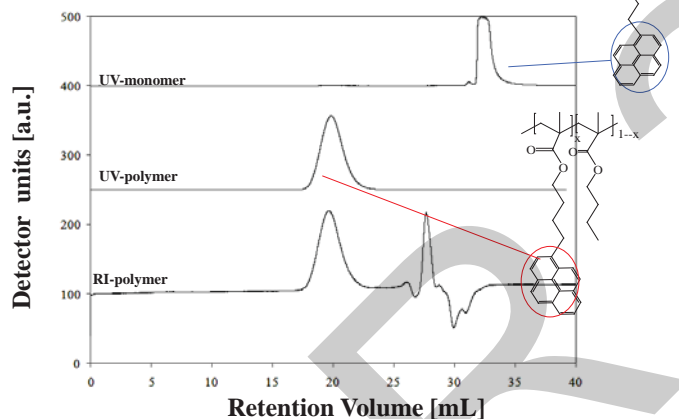
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2. Sample Preparation

GPC Characterization



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2. Sample Preparation

Number-average molecular weights (M_n) and polydispersity indices (PDI) of the Py-labelled samples

PC ₁ A			PC ₁ MA			PC ₄ MA		
Pyrene Content [mol %]	Mn [g/mol]	PDI [-]	Pyrene Content [mol %]	Mn [g/mol]	PDI [-]	Pyrene Content [mol %]	Mn [g/mol]	PDI [-]
0.3	265,000	1,38	0.3	134,000	1.70	0.3	174,000	1.93
2.6	236,000	1,40	1.3	130,000	1.42	1.1	272,000	1.99
2.6	313,000	1,40	2.7	200,000	1.33	2.2	296,000	1.44
3.0	173,000	1.42	4.0	135,000	1.60	3.0	197,000	1.39
5.0	138,000	2.08	5.3	206,000	1.70	3.6	264,000	1.68
6.2	145,000	1,38	5.6	170,000	1.55	5.3	275,000	1.97
6.7	870,000	2.40	7.3	176,000	1.80	7.2	416,000	1.76

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2. Sample Preparation

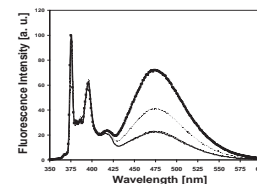
- polymer chain dynamics (PCD) of actual polymers are being compared as a function of the polymer chemical composition

PC ₈ MA			PC ₁₂ MA			PC ₁₈ MA		
Pyrene Content [mol %]	Mn [g/mol]	PDI [-]	Pyrene Content [mol %]	Mn [g/mol]	PDI [-]	Pyrene Content [mol %]	Mn [g/mol]	PDI [-]
0.4	244,000	1.87	0.5	530,000	1.72	0.7	563,000	1.45
1.8	305,000	1.88	1.4	265,000	1.70	1.4	810,000	1.54
2.7	312,000	1.75	3.5	244,000	2.43	4.5	480,000	1.52
4.3	146,000	2.04	5.6	507,000	1.70	5.9	663,000	1.44
5.1	371,000	1.83	6.0	174,000	2.17	6.8	705,000	1.42
6.1	234,000	1.88	7.7	662,000	2.10	6.7	719,000	1.41
7.3	271,000	2.07	10.2	265,000	1.68	14.2	770,000	1.49

3. Analysis

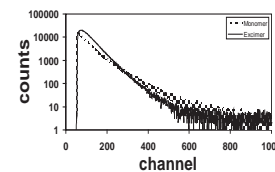
1. Steady-state fluorescence spectroscopy

continuous excitation at 344 nm
 emission spectrum: 350-600 nm



2. Time resolved fluorescence

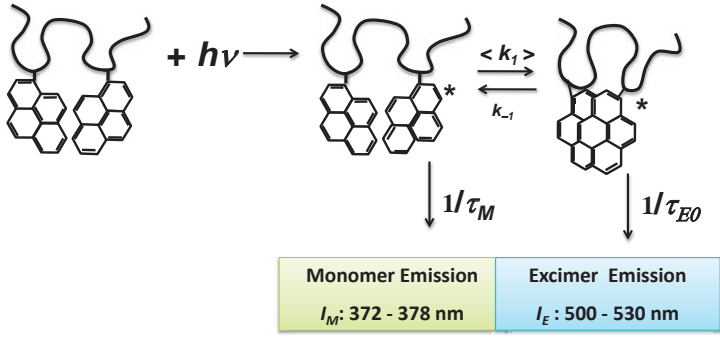
excitation: single light pulse at 344 nm
 emission wavelength scanned: 375 nm, 510 nm



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3. Analysis

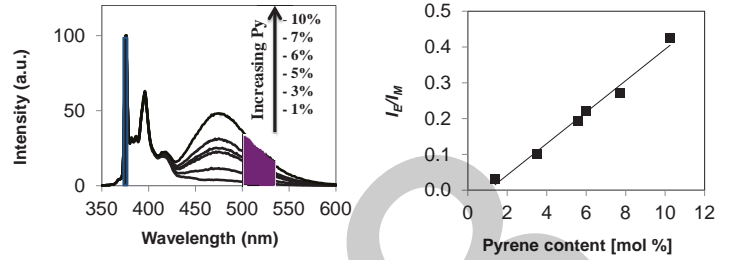
Kinetics for pyrene excimer formation



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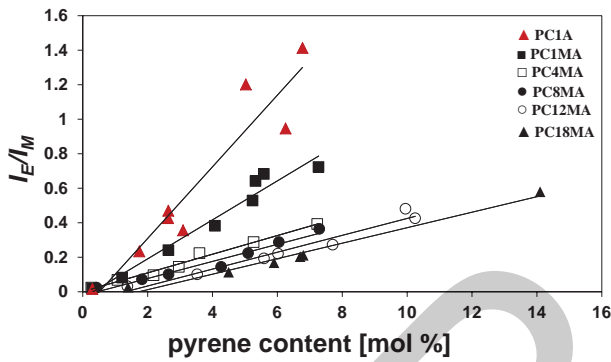
4. Results

- steady state fluorescence spectroscopy of PC12MA



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4. Results - I_E/I_M ratios

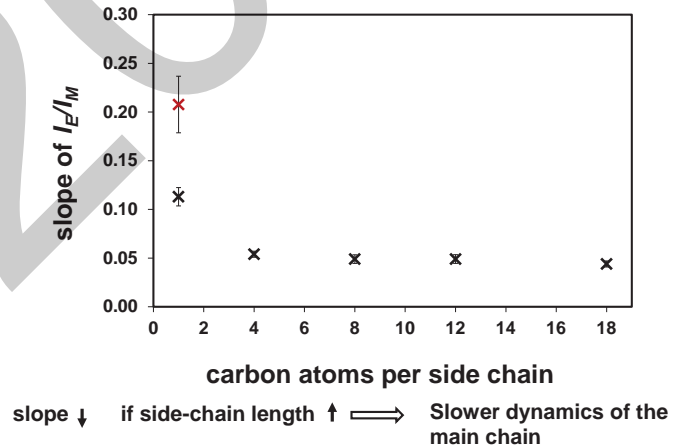


Steady-state data: excimer formation \downarrow if side-chain length \uparrow

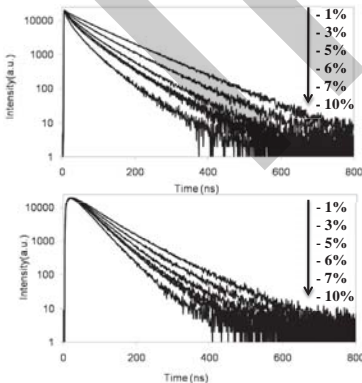
Explanation: backbone flexibility \downarrow if side chain-length \uparrow

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4. Results



4. Results - Time resolved fluorescence spectroscopy



Monomer
 $\lambda_{ex} = 344$
 $\lambda_{em} = 375$

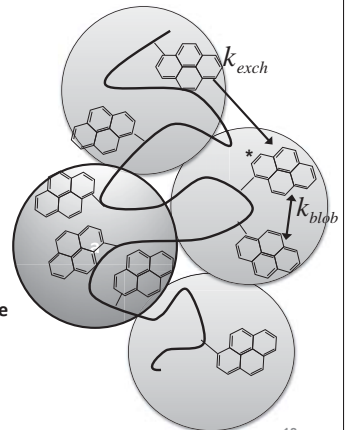
Excimer
 $\lambda_{ex} = 344$
 $\lambda_{em} = 510$

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The Fluorescence Blob Model (FBM)

• FBM Parameters:

- k_{blob} : Excimer formation rate constant in a blob containing one excited and one ground-state pyrene
- $\langle n \rangle$: Average number of ground-state pyrenes per blob
- k_{exch} : Exchange rate constant of ground-state pyrenes between blobs
- N_{blob} : The blob size in number of monomer units
- $\langle k_{blob} \times N_{blob} \rangle$: represents the average rate constant of excimer formation for the polymer in a given solvent



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The Fluorescence Blob Model

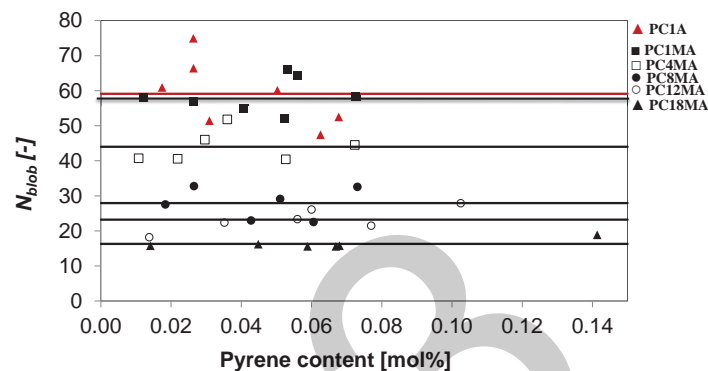
- By fitting fluorescence decays using the FBM equations, the important parameters can be obtained

$$N_{blob} = \frac{\langle n \rangle}{\left(\frac{\lambda}{f_{diff}} \right) [M_2 x + M_1 (1-x)]}$$

- Using $\langle n \rangle$, can calculate the blob size N_{blob} , in number of monomer units per blob:
- The average of the product $\langle k_{blob} \times N_{blob} \rangle$: at each pyrene content, represents the rate constant of excimer formation throughout the polymer in a given solvent

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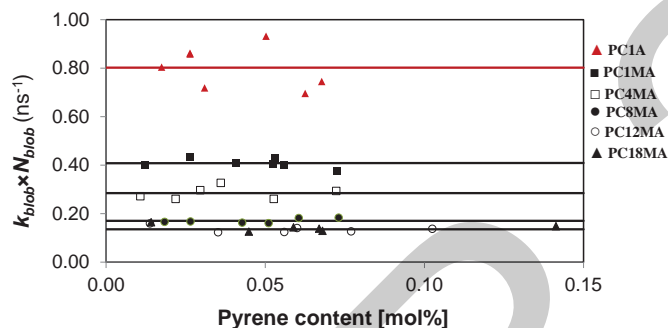
5. Results



- $N_{blob} \downarrow$ if side-chain length \uparrow
 \rightarrow backbone flexibility \downarrow if side-chain length \uparrow

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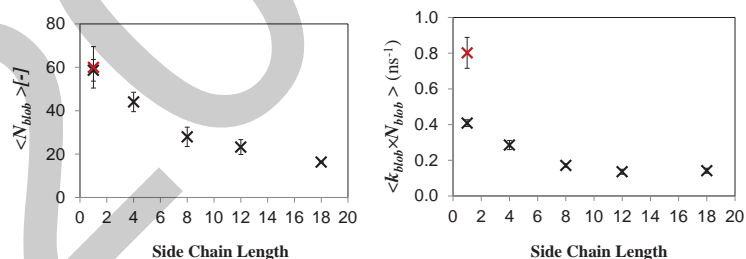
5. Results



- $k_{blob} \times N_{blob} \downarrow$ if side-chain length \uparrow
 \rightarrow backbone flexibility \downarrow side chain length \uparrow

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5. Results - Summary



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6. Summary

- Pyrene labelled PC1MA, PC4MA, PC8MA, PC12MA, and PC18MA were synthesized and characterized.
- Steady-state results showed an increase in the ratios of I_E/I_M with increasing pyrene content.
- Time-resolved fluorescence of monomer and excimer were conducted for each sample.
- The FBM was applied to the fluorescence decays of each sample.
- The FBM analysis describe quantitatively the flexibility of a given polymer chain which demonstrated that we have a tool to calculate the dynamic.

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Future work

- Use of this study as a reference for other polymers chain dynamic studies.
- The results in this study is expected to become a reference for protein chain dynamics influenced by the bulkiness of different side-chains.

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Acknowledgements

- Dr. Jean Duhamel
- Dr. Mario Gauthier, Dr. Neil McManus, Dr. Xiaosong Wang
- Manoj Mathew
- Henning Weiss
- Duhamel and Gauthier Group
- Funding provided by NSERC



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THANK YOU

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IPRR 2013