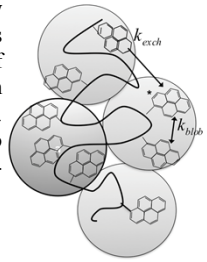
Effect of Side Chain Length on the Internal Dynamics of Polymethacrylates in Solution

Shiva Farhangi, Henning Weiss, Jean Duhamel

Institute for Polymer Research, Department of Chemistry, University of Waterloo
200 University Avenue West, Waterloo, Ontario, N2L 3G1, Canada

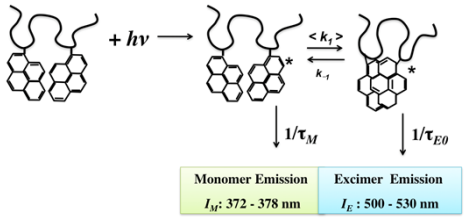
Introduction

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. This study uses pyrene excimer formation to probe the internal dyanmics of several pyrene-labeled poly(methacrylates).



Mechanism

The Kinetics for Pyrene excimer formation



hν is the energy of one photon

k_1 is the excimer formation rate constant

k_{-1} is the excimer dissociation rate constant

τ_M is the lifetime of the monomer

τ_{E0} is the lifetime of the excimer

Sample Preparation

Poly(methacrylates) randomly labeled with pyrene;

Radical copolymerization: 1-Pyrenebutyl methacrylate + Monomer

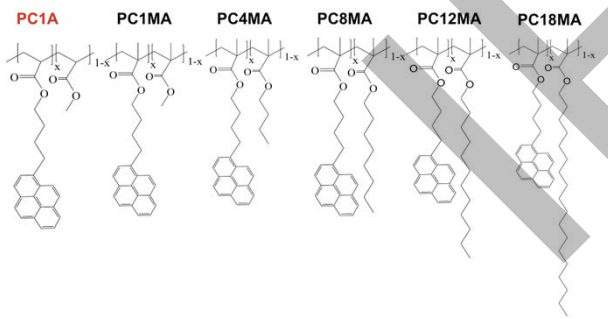


Figure 1: Chemical structures of PC1A, PC1MA, PC4MA, PC8MA, PC12MA, PC18MA.

Molecular Weight and PDI

Py-PC1A			Py-PC1MA			Py-PC4MA		
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
Py-PC8MA			**Py-PC12MA**			**Py-PC18MA**		
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	1.54
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

Table-1: Molecular Weight and PDI of PC1A, PC1MA, PC4MA, PC8MA, PC12MA, and PC18MA obtained by GPC.

Results and Discussion

The steady-state fluorescence spectra and time-resolved fluorescence decays acquired for a series of Py-PC12MA samples with different pyrene content ranging from 1-10 mol% are shown in Figure 1.

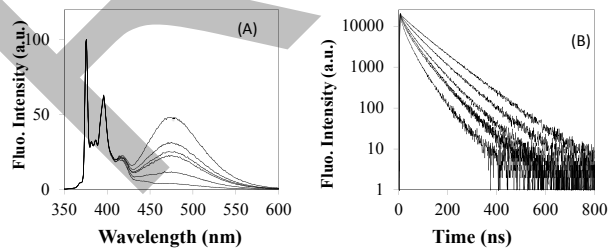


Fig. 1. Steady-state fluorescence spectra of Py-PC12MA in THF; Pyrene content decreased from top (10 mol%) to bottom (1 mol%). B) Time-resolved fluorescence decay of Py-PC12MA in THF. Pyrene content increased from bottom.

As the pyrene content of the polymer increases, more excimer is being formed as shown in the fluorescence spectra. The fluorescence decays of the pyrene monomer are shorter-lived reflecting enhanced excimer formation.

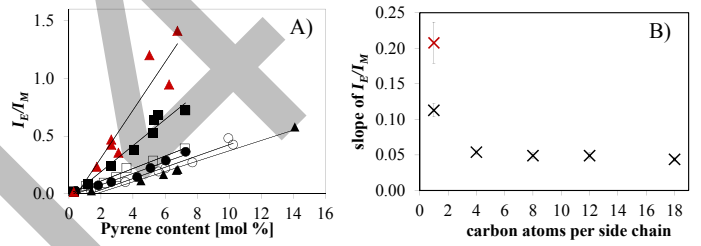


Fig. 2. A) I_E/I_M ratios for all polymers with increasing pyrene contents; ▲P1MA, ■PC1MA, □PC4MMA, ●PC8MMA, ○PC12MMA, ▲PC18MMA. B) Slope of the I_E/I_M of PC1A, PC1MA, PC4MA, PC8MA, PC12MA, and PC18MA . The slope reaches a plateau as the side chain length increased from C4-C18.

I_E/I_M increases linearly with increasing pyrene content, but the slope decreases with increasing side-chain length due to slower internal dynamics of the main chain. Quantitative information about the changes in internal dyanmics are obtained from the global analysis of the fluorescence decays according to the Fluorescence Blob Model (FBM).

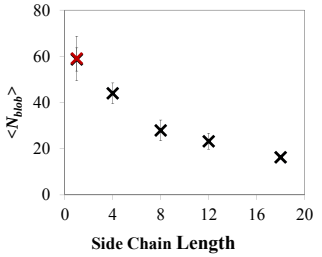


Fig. 3. $<N_{blob}>$ values for pyrene labeled copolymers as a function of side-chain length. × polymethacrylates, × polyacrylate

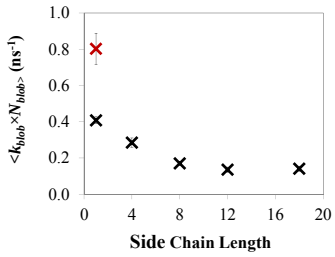


Fig. 4. $<N_{blob}>$ values for pyrene labeled copolymers as a function of side-chain lengths; × polymethacrylates, × polyacrylate

Conclusion

Pyrene labelled PC1A, PC1MA, PC4MA, PC8MA, PC12MA, and PC18MA were synthesized. The fluorescently labelled polymer samples were studied using steady-state and time-resolved fluorescence. Two important parameters, namely N_{blob} and $k_{blob}\times N_{blob}$, were determined with the FBM analysis. For each polymer series, both N_{blob} and $k_{blob}\times N_{blob}$ remained constant within experimental error with pyrene content, but their average value $<N_{blob}>$ and $<k_{blob}\times N_{blob}>$ 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.

Acknowledgements

The authors thank NSERC for generous support.