IPR

Institute for Polymer Research

Characterization of the Distribution of Pyrene Pendants Attached onto a Polymer

Mark Ingratta, Jean Duhamel

Chemistry Department
University of Waterloo

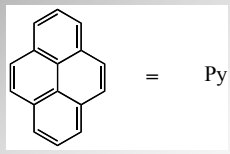
IPR Symposium
May 16, 2006

Outline

- Background
- Purpose
- The Fluorescence Blob Model
- Synthesis of Polystyrenes
- Results
- Conclusions

Background

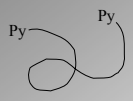
- Polymer behavior in solution is studied extensively using pyrene fluorescence
- Associative thickeners, viscosity modifiers
- Use Excimer formation used to determine dynamics



= Py

Typical Fluorescence Studies on Polymers using Pyrene

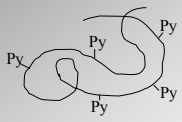
- End-to-end cyclization



Advantages/ Disadvantages

- Well-defined system
- Quantitative results
- Limited to shorter chains

- Random labeling of entire chain



- Unlimited chain length
- Poorly defined system
- Typically, more qualitative results

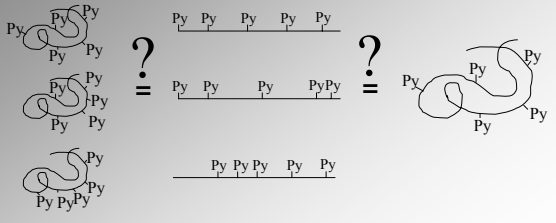
Question?

- More and more quantitative work is being done on "randomly labeled" polymers
- Regardless of the method of incorporation, the fluorescent pendants are assumed to distribute themselves randomly inside the polymer coil.

Question: Is it true?

Goal

- To determine if the method of incorporation will affect how pendant groups are distributed in a 3-D polymer coil



Various distributions in 3-D

Various distributions in 1-D

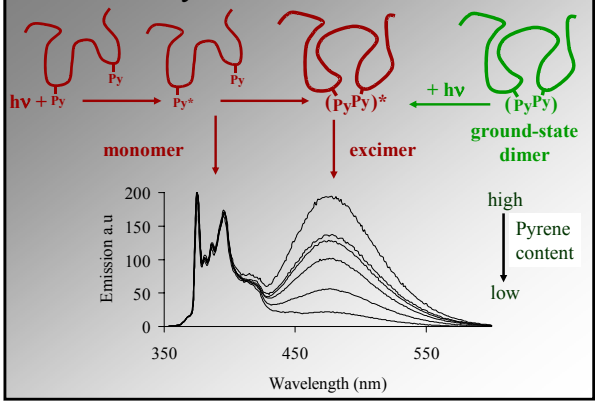
Same distribution in 3-D

How?

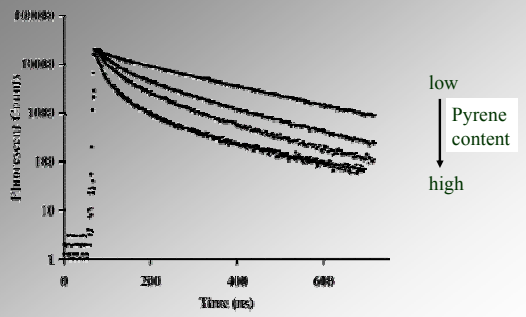
- Prepare three series of polystyrenes with pyrene incorporated in different ways
- Use excimer formation to evaluate the distribution of pendants inside the polymer coil
- Using the florescence blob model, we can quantify the dynamics of the chain

Fluorescence Background

Pyrene Fluorescence

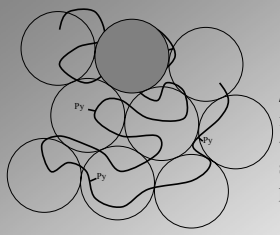


Time-Resolved Fluorescence



Fluorescence decays of the pyrene monomer for Py-PGA.
Duhamel, J.; Kanagalingam, O'Brien, T. J.; Ingratta, M. W.; *Journal of the American Chemical Society*, **2003**, *125*, 12810-12822.

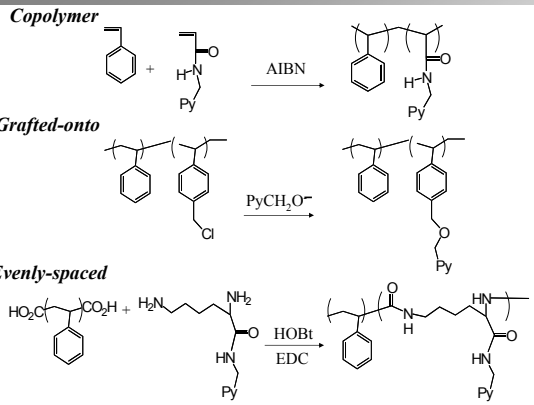
Polymer ⟶ Blobs



k_{blob} = rate constant for excimer formation by diffusion
$\langle n \rangle$ = average number of ground state pyrenes per blob (quenchers per blob)

$k_e[blob]$ = rate of pyrene exchange between blobs × blob concentration per polymer coil
N_{blob} = number of units per blob

Materials:

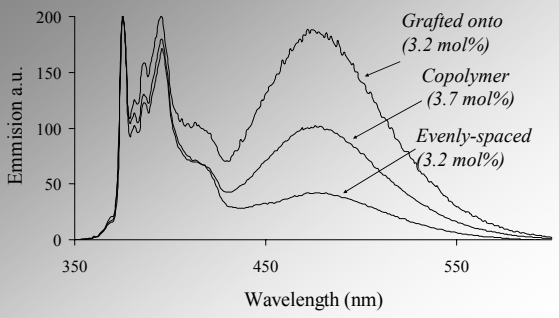


Results

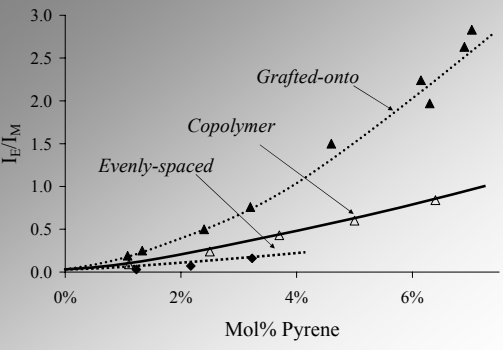
Pyrene labeled Polystyrenes

- *Evenly-spaced* polystyrene
  - pyrene content 1-3 mol%
- *"Randomly" Labeled* polystyrene
  - *Grafted-onto*: pyrene content 1-7 mol%
  - *Copolymer*: pyrene content 1-7 mol%

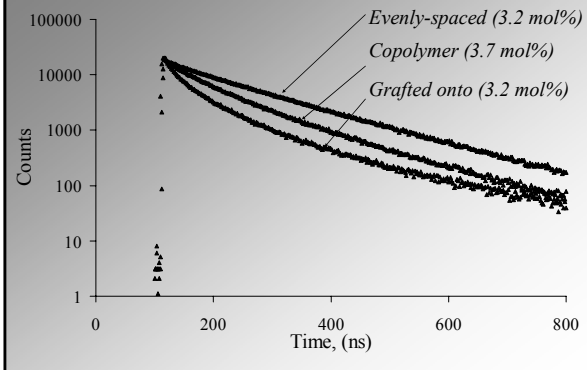
Steady-State Spectra



Comparison of Pyrene I_E/I_M

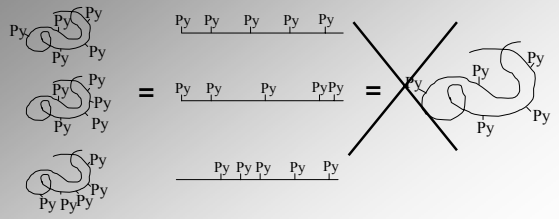


Time-Resolved Decays

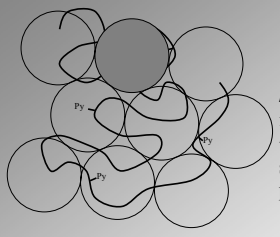


Conclusion

- The fluorescent results for all three series of polymers is clearly different!!



Polymer ⟶ Blobs



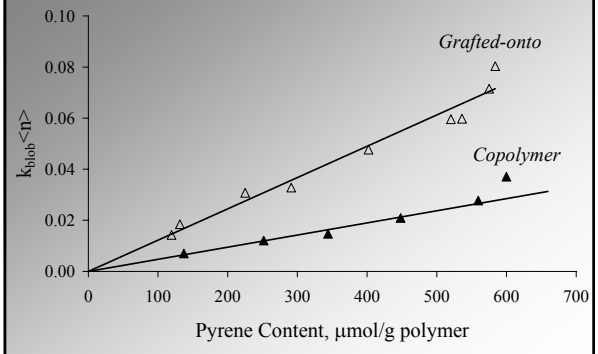
k_{blob} = rate constant for excimer formation by diffusion
$\langle n \rangle$ = average number of ground state pyrenes per blob (quenchers per blob)

N_{blob} = number of units per blob

Local Pyrene Concentration

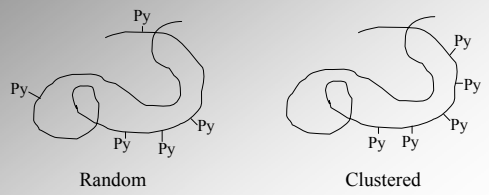
- k_{blob}^{-1} is proportional to V_{blob}
- <n> is the average number of pyrenes per blob
- Therefore, $k_{blob} \times \langle n \rangle$ represents the *local* pyrene concentration
- We expect that the local pyrene concentration should increase with pyrene content

Local Pyrene Concentration



Comparing Pyrene Content

- Pyrene content and *local* pyrene content do not agree
- Why? Clustering of pyrene groups would artificially increase the local pyrene content

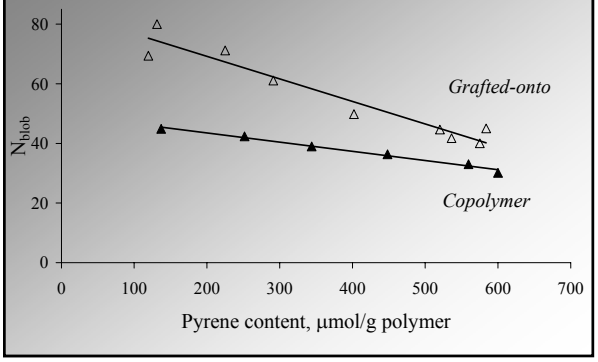


Effect of Clustering on N_{blob}

- As clustering increases, <n> increases
- <n> is directly linked to N_{blob}

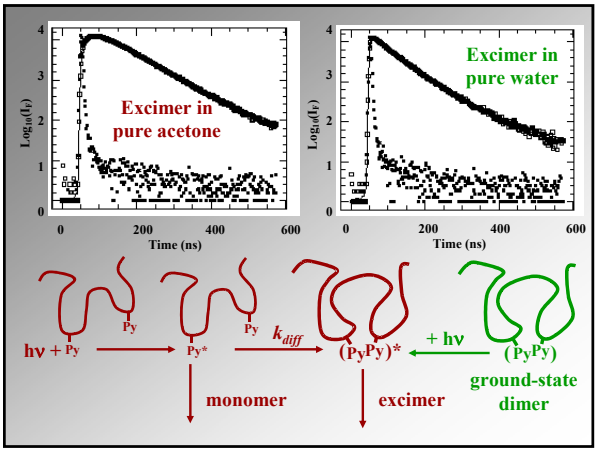
$$N_{blob} = \frac{\langle n \rangle}{\lambda / f \left[PyAAm(x) + Sty(1-x) \right]}$$

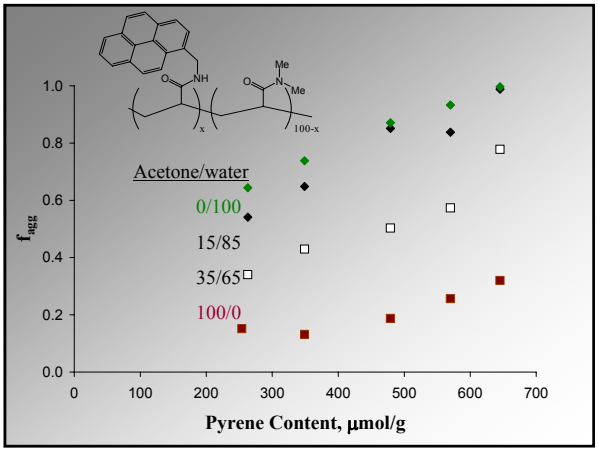
N_{blob} vs. Pyrene content



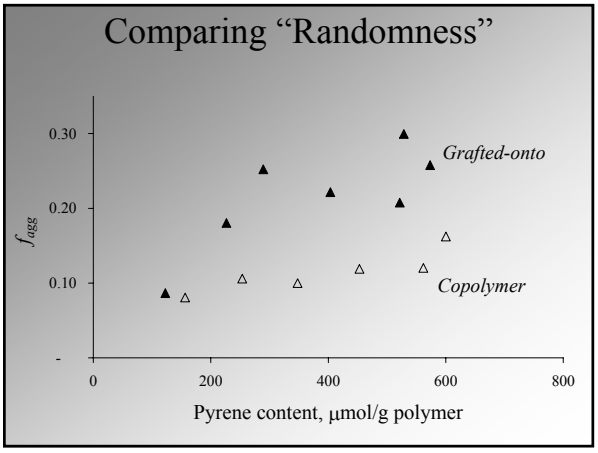
Solution

- We need to define the level of clustering
- f_{agg} is a quantitative measure of the amount of ground state excimers
- The more ground state excimers present, the more aggregated/clustered the pendants are.
- Compare to "model system" of Poly(dimethylacrylamide); (PDMA)

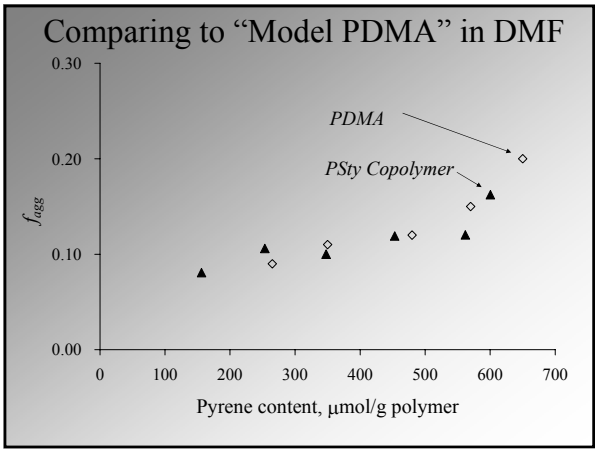




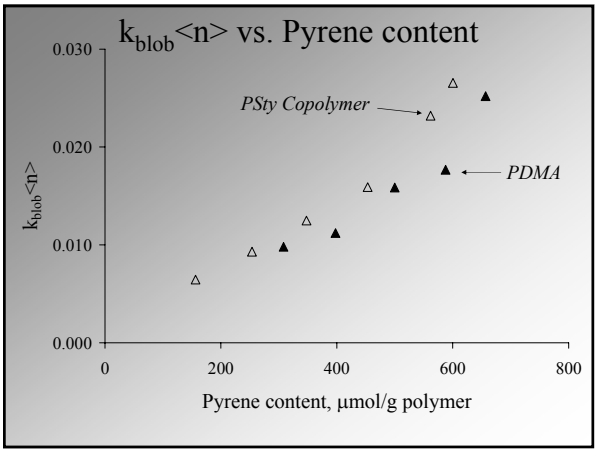
Comparing "Randomness"



Comparing to "Model PDMA" in DMF



$k_{blob}\langle n\rangle$ vs. Pyrene content



Conclusions

- Three series of pyrene labeled polystyrenes were studied using fluorescence
- It was discovered that the method of labeling has an effect on the results obtained
- Through use of the fluorescence blob model, the pyrene labeled polymers can still be studied

Acknowledgements

- Supervisor, Jean Duhamel
- Lab Colleagues
- OGSST, NSERC

Questions / Comments ??