Long Range, Polymer Chain Dynamics of a "Stiff" Polymer. Fluorescence from Poly(isobutylene-*alt*-maleic anhydride) with *N*-(1-Pyrenymethyl) succinimide Groups

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Introduction

The ability to probe long range polymer chain dynamics (LRPCD) allows researchers to quantify the stiffness of a polymer. Traditionally LRPCD of a polymer is determined by end labeling a polymer with two chromophores and measuring the end-to-end cyclization (EEC) rate constant, k_{cy}. However, this procedure is limited to polymers which are flexible enough to cyclize while the chromophore remains excited.

Poly(isobutylene-*alt*-maleic anhydride) (PIMA) is an alternating copolymer of isobutylene and maleic anhydride. The anhydride groups are expected to stiffen the PIMA backbone and as a result, PIMA would not be a good candidate to characterize its LRPCD by EEC experiments.

Excimer formation between two pyrene labels covalently and randomly attached onto a macromolecule can be applied to characterize LRPCD since it will be related to the flexibility of the polymer. Steady-state (SS) and time-resolved (TR) fluorescence can be used to determine the efficiency of pyrene excimer formation from the ratio of excimer to monomer fluorescence, namely the I_E/I_M ratio, and the rate constant, k, of pyrene excimer formation.

PIMA was reacted with 1-pyrenemethylamine to obtain five randomly labeled polymers (Py-PIMA).

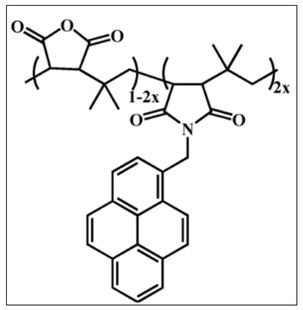

Figure 1: Monomer unit of Py-PIMA polymers which contain 0.5, 5, 10, 25 and 47.5 molar percentage of pyrene with respect to the number of structural units.[1]

To demonstrate that the LRPCD of Py-PIMA in THF could be obtained, the SS spectra were acquired and the TR decays were analyzed using the model free analysis (MFA).

Results

The SS florescence spectra in Figure 2 show an increase in the intensity of excimer at 480 nm as the molar percentage of pyrene increased.

By applying the model free analysis (MFA) to the monomer and excimer decays, $\langle k^{MF}\rangle_{blob}$ was calculated and compared for each of the randomly labeled Py-PIMA polymers. The value was shown to remain constant within experimental error, as shown in Figure 3, confirming that the addition of 1-pyrenemethylamine does not alter the LRPCD of PIMA.

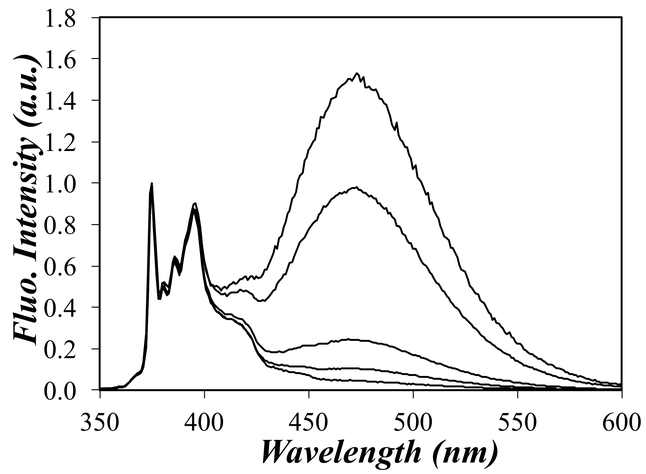

Figure 2: SS fluorescence spectra of the Py-PIMA samples normalized at 375 nm. From bottom to top: 0.5, 5, 10, 25 and 47.5 ml% of pyrene with respect to the number of structural units.[2]

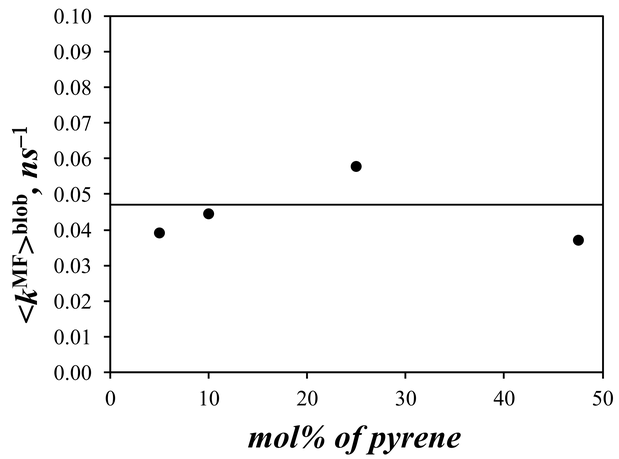

Figure 3: $\langle k^{MF}\rangle_{blob}$ as a function of molar percentage of pyrenyl-labeled structural units.[2]

The value of $\langle k^{MF}\rangle_{blob}$ was then compared in Figure 4 to that obtained for pyrene labeled poly(styrene) and a series of poly(alkyl methacrylates) as a function of the molar mass of the structural unit. It can be seen that $\langle k^{MF}\rangle_{blob}$ for Py-PIMA takes a much lower value than that obtained for different pyrene-labeled polystyrene constructs (PyMeN-X(3)-PS or PyBut-X(6)-PCyMA series) which have a similar molar mass for the structural unit. The samples with a hollow circles were prepared with 1-pyrenylbutyl which has a longer spacer between pyrene and the backbone compared to the linker used to synthesize the Py-PIMA sample. Shortening the pyrene linker has been shown to decrease

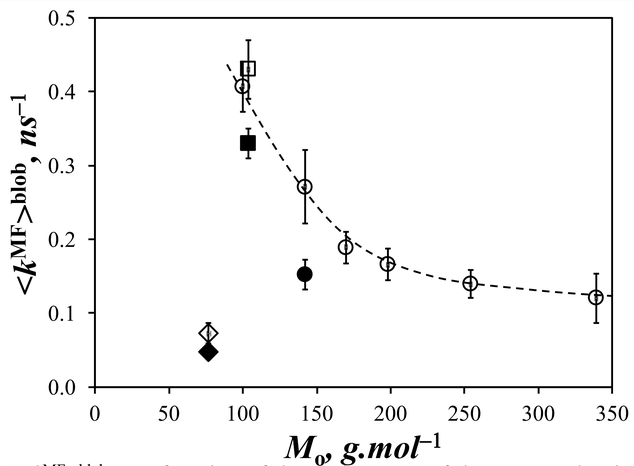

Figure 4: $\langle k^{MF}\rangle_{blob}$ as a function of the molar mass of the structural unit (M_0): (○) PyBut-X(6)-PCyMA series with y = 1, 4, 6, 8, 12, and 18; (●) PyMeO-X(3)-PC4MA; (□) PyBut-X(6)-PS; (■) PyMeN-X(3)-PS; (◆) Py-PIMA; (◇) Py-PIMA scaled by 1.54.[2]

$\langle k^{MF}\rangle_{blob}$; therefore to account for the effect that the linker length has on $\langle k^{MF}\rangle_{blob}$. the value obtained for Py-PIMA was scaled by 1.54 (hollow diamond).[3]

Conclusions

In conclusion, the LRPCD of Py-PIMA has been successfully quantified and is shown to be extremely slow compared to other polystyrene and poly(alkyl methacrylate) samples.

References

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2) Thoma, J. L., Duhamel, J., Li, M. J., Bertocchi, M. J., & Weiss, R. G. Long-Range, Polymer Chain Dynamics of a "Stiff" Polymer. Fluorescence from Poly (isobutylene-*alt*-maleic anhydride) with *N*-(1-Pyrenylmethyl) succinimide Groups. *Macromolecules* **2017**, ASAP.
3) Farhangi, S.; Duhamel, J. Probing Side Chain Dynamics of Branched Macromolecules by Pyrene Excimer Fluorescence. Macro- molecules 2016, 49, 353−361.

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